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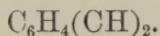
DECEMBER 1926.

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CIX. *X-ray Examination of the Crystal Structure of Certain Compounds.* By A. NATH SARKAR, Ph.D.\*

[Plates XXI. & XXII.]

(A) CATECHOL.



WHEN two hydrogens of benzene are replaced by two hydroxyl-groups, three isomeric compounds, catechol, resorcinol, and quinol, are formed.

The first compound of this group, catechol, was taken for examination by the "powder" method. Crystals of catechol grown from an aqueous solution were in the form of thin plates. The forms developed were  $a$  (100),  $m$  (110),  $c$  (001), and probably  $x$  (121); the faces of large area were  $a$  (100) faces.

Groth describes the crystal as follows:—

"Monoclinic prismatic.

$$a:b:c = 1.6086 : 1 : 1.0229; \quad \beta = 95^\circ 15';$$

$$\Delta = 1.367 - 1.375."$$

(*Chemische Krystallographie*, vol. iv. p. 84.)

Since this crystal belongs to the prismatic class, the possible number of molecules per cell is either 1, 2, 4, 8, or 16.

The spacings of the 3 axial planes corresponding to these five possible values of  $H$ , calculated from the crystallographic

\* Communicated by Prof. Alfred W. Porter, D.Sc., F.R.S.

data and density 1.37 (mean value), are shown below :—

TABLE I.

N.	a-spac.	b-spac.	c-spac.
1 .....	6.93 Å.	4.34 Å.	4.45 Å.
2 .....	8.74 „	5.47 „	5.60 „
4 .....	11.01 „	6.90 „	7.07 „
8 .....	13.86 „	8.68 „	8.90 „
16 .....	17.48 „	10.84 „	11.20 „

One of the "powder" photographs of this crystal obtained by using the K-characteristic rays of copper is shown (Pl. XXI.). The distance of the plate from the crystal powder was 3.48 cm. The spacings of the 17 diffraction lines occurring on the plate were calculated in the usual manner, and are given in the third column of the following table :—

TABLE II.

No. of line.	INT.	Obs. spac.	Calc. spac. N = 2.	Indices of Planes.	Remarks.
1.....	VS	8.73	8.74	100	
2.....	S	5.42	5.47	010	
3.....	VS	4.73	4.62	110	
4.....	W	4.38	—	—	2nd-order 100; sp. = 8.74.
5.....	MS	3.82	3.89	011	
6.....	M	3.69	3.65	111	
7.....	VVS	3.42	3.42	210	
8.....	MS	2.98	3.00	211	
9.....	WM	2.90	—	—	or 3rd-order 100; sp. = 8.74.
10.....	W	2.71	2.73	102	or 2nd-order 010; sp. = 5.47.
11.....	MS	2.64	2.60	120	or 102; sp. = 2.58.
12.....	WM	2.44	2.47	012	or 021; sp. = 2.45.
13.....	M	2.31	2.33	121 or 112	or 2nd-order 110 (this line is wide and looks double).
14.....	WM	2.07	2.08	302	
15.....	VVV	2.02	2.03	410	
16.....	VW	1.85	—	—	2nd-order 111 (7); sp. = 3.65.
17.....	M	1.81	—	—	2nd-order 201 (rather wide); sp. = 3.59.

The above table shows that the spacings of the planes corresponding to the first two lines on the plate agree with the full calculated spacings of the planes  $a$  (100) and  $b$  (010) corresponding to 2 molecules per cell.

As this suggested the probability of the number of molecules per cell being 2, the spacings of all simple planes were calculated on this assumption from the crystallographic data and mean density of the crystal as given by Groth. The comparison of the observed and calculated spacings shows that the presence of all the 17 lines could be accounted for.

*Basic Lattice.*—Table II. shows that the only axial plane which has its spacing abnormally reduced is  $c$  (001). This clearly shows that the basic lattice of the crystal cannot be  $\Gamma m'$ , for the abnormal spacings that arise out of each of the three cases of  $\Gamma m'$  are the halvings of the spacings of all planes  $(hkl)$  when either  $(h+k)$ ,  $(k+l)$ , or  $(h+k+l)$  is odd; so that each of them involves the halving of the spacings of at least two of the three axial-plane's spacings.

*Space-Group.*—The table further shows that planes (001), (101), (10̄1), (201), (20̄1), etc., i.e. planes  $(hol)$  when  $l$  is odd, do not produce lines at their full calculated spacings. Spacings of these planes can be halved (no other fraction being possible since the basic lattice of the crystal is  $\Gamma m$ ) only if the symmetry-plane is a glide-plane and its translation parallel to its own plane is  $\frac{c}{2}$ . Since the basic lattice is  $\Gamma m$ ,

the symmetry-plane is a glide-plane, the number of molecules per cell is 2, and the spacing  $b$  (010) is not halved, the axis of the symmetry cannot be a screw-axis. The space-group therefore is  $C_{2h}^4$ .

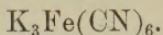
From the above it follows that the molecules should possess an element of symmetry which in the present case can be either a centre of symmetry or an axis of binary symmetry.

The data given by the "powder" photograph of the crystal are not sufficient for fixing the relative positions of the two types of molecules in the unit cell, or for the differentiation between the two alternative types of possible molecular symmetry.

Since the translation of the glide-plane parallel to itself is  $\frac{c}{2}$  and the number of molecules per cell is 2, the molecules are most densely packed in the  $a$  (100) plane. This accounts

for the presence of the diffraction lines corresponding to the 1st-, 2nd- and 3rd-order reflexions from this plane being present on the plate, and also the cleavage plane of this crystal being parallel to  $a(100)$  on the assumption that cleavage follows the direction of a plane of high molecular density.

### (B) POTASSIUM FERRICYANIDE.



Crystals of potassium ferricyanide belong to the monoclinic prismatic class. The forms commonly developed are  $a(100)$ ,  $x(322)$ ,  $w(1\bar{1}\bar{1})$ ,  $q(011)$ ,  $V(1\bar{2}\bar{2})$ ,  $o(111)$ , and  $m(110)$ . The plane of cleavage is parallel to  $a(100)$ .

The crystallographic data given by Groth are as follows :—

$$“a:b:c = 1.287:1:1.8013; \quad \beta = 90^\circ 6' ;$$

$$\Delta = 1.849 - 1.861.”$$

(Groth, *Chem. Krys.* vol. i. p. 420.)

A thin plate of the crystal with large  $a(100)$  faces was selected for X-ray examination by the Laue method. The crystal was so mounted that the incident beam was normal to the  $(100)$  face and the  $b$ -crystallographic axis vertical. The distance of the plate from the crystal was 4 cm.

The source of X-rays was a Coolidge tube with a tungsten anticathode, and the tube was run at a voltage of 60 K.V. The photograph obtained is shown in (Pl. XXI.). The number of spots occurring on the plate is comparatively few, though the length of exposure was over 30 hours. This is probably due to the fact that this compound contains both iron and potassium, so that a wide band of the spectral range which was being used was very highly absorbed in the crystal. The symmetry of the pattern is two-fold about the horizontal line of the photograph (parallel to the  $c$ -axis of the crystal), and characteristic of the Laue diagrams of crystals belonging to the cyclic group when the X-rays are incident normally on a crystal face containing the symmetry-axis.

The spots which lie on the horizontal line are due to planes of the type  $(hol)$  and  $(h\bar{o}\bar{l})$ . The glancing angles for the planes reflecting these spots were obtained from their distance from the centre of the photograph, and the probable indices of the reflecting planes fixed by comparison of the observed values of the glancing angles with those calculated for the

above types of planes from the crystallographic data given by Groth\*.

The identification of the spots is shown in the following table; the indices of the planes (referred to Groth's ratio) are given in the 4th and 9th columns.

TABLE III.

Spots on + side of <i>c</i> -axis.					Spots on - side of <i>c</i> -axis.				
INT.	Obs. <i>θ</i> .	Calc. <i>θ</i> .	Indices of Planes.	Correct Indices.	INT.	Obs. <i>θ</i> .	Calc. <i>θ</i> .	Indices of Plane.	Correct Indices.
VS ...	6° 25'	6° 20'	106	103	VS ...	5° 31'	5° 49'	106	101
Abs ...	—	8° 59'	104	102	Abs ...	—	8° 44'	104	102
W ...	11° 9'	10° 58'	3.0.10	305	W ...	9° 54'	10° 11'	3.0.10	305
VS ...	17° 50'	17° 21'	102	101	VS ...	16° 58'	17° 9'	102	101
Abs ...	—	24° 52'	304	302	Abs ...	—	24° 20'	304	302

In the foregoing table we observe that the plane (102) produces a very strong spot, but no spot occurs corresponding to the plane (304). This seems unaccountable (unless the reflexion from 304 is naturally very weak), for any geometrical arrangements of molecules which will abnormally reduce the spacing of (304) will also affect (102) in a similar manner. We also find that not only are the spots corresponding to the planes (103) and (105) absent, but that no spot is reflected at the proper angle for (104). The two alternative solutions suggested by the absence of reflexions from (103) and (105) cannot account for the absence of spots corresponding to the planes (104) and (304) as well. Furthermore, the total absence of a spot due to (104) cannot be attributed to the plane reflecting rays which are too weak to produce an appreciable effect on the plate, for the spacing and glancing angles for this plane are intermediate between those of (102) and (106), both of which produce strong Laue spots. It is also equally impossible to account for the total absence of reflexion from (104) on the supposition that the wave-lengths which could have contributed

\* For  $\theta_{hol} = \cot^{-1} \left\{ 1.608 \frac{1}{h} + .0016 \right\} + 6'$ ,

$\theta_{hol} = \cot^{-1} \left\{ 1.608 \frac{1}{h} - .0016 \right\} - 6'$ .

mostly to the intensity of the spot fall within the band of the incident beam which is highly absorbed in the crystal, because this band lies in the region of comparatively long wave-lengths.

These anomalous results can be consistently reconciled if we assume that the ratio of  $b : c$  as given by Groth should be doubled (*i.e.* the true ratios are  $a : b : c = 1.287 : 1 : .4013$ ). The various reflecting planes are re-indexed according to the corrected axial ratios in the 5th and 10th columns of Table III. According to the corrected axial ratios we find that the spots corresponding to the planes (102) and (302) are absent, whereas planes (103), (101), and (305) produce Laue spots. These abnormal reflexions are no longer anomalous, for they can arise out of either of the following cases :—

- (1) The plane of symmetry is a glide-plane, and the translation of the glide-plane parallel to itself is  $\left(\frac{a}{2} + \frac{c}{2}\right)$ . This will halve the spacings of all planes ( $hkl$ ) when  $(h+l)$  is odd.
- (2) The basic lattice is the body-centred second lattice  $\Gamma m'$ , when the spacings of all planes ( $hkl$ ), for which  $(h+k+l)$  is odd, are halved.

The indices of the planes which reflect the Laue spots lying on the vertical line through the centre of the photograph are of the type ( $hko$ ). The spacings of all such planes are unaffected by case (1), but case (2) will affect some of them. The two alternative cases may therefore be differentiated from the study of indices of this type of planes and the intensity of the spots reflected by them.

Table IV. shows the identification of the 5 spots which lie on the positive side of the vertical line throughout the centre.

TABLE IV.

INT.	Obs. $\theta$ .	Calc. $\theta$ .	Indices of Plane.
W .....	8° 53'	8° 50'	150
M .....	10° 49'	11° 0'	140
VS .....	14° 25'	14° 23'	130
M .....	17° 15'	17° 15'	250
M .....	21° 7'	21° 14'	120

We thus find that the reflexions from all simple planes 150.....120, whether  $(h+k+l)$  is odd or even, are present. This suggests the probability of the basic lattice not being  $\Gamma m'$ ; but, as the intensity of the spots due to the planes (140), (250), and (120) is weaker than that due to (130), it is just possible that odd-order reflexions from the three former planes are really absent and the corresponding spots are due to even-order reflexions.

To settle this point definitely a gnomonic projection was made from the Laue diagram. The indices of the reflecting planes calculated from the projection did not show any indication of the halving of the spacings of planes  $(hkl)$  when  $(h+k+l)$  is odd, either by the absence or by the comparative weakness of the spots reflected from such planes generally.

It was therefore concluded that the basic lattice of the crystal is  $\Gamma m$ . (Results given later in Table V. also confirm this conclusion.)

The method adopted in this case for the determination of the number of molecules per cell requires a general idea of the relative energy in different parts of the incident radiation, and their photographic effect. They are briefly described below.

Dauvillier \* observed that when the source of X-rays is a glass bulb, wave-lengths longer than  $1\cdot5$  Å. are entirely absorbed by the thick glass walls. The general radiation curve for 60 K.V. obtained by Hull and Rice † using a Coolidge bulb with a tungsten target shows that the relative energy of the rays longer than  $9$  Å. is very small. In the present case we can assume the contribution of wave-lengths longer than  $9$  Å. to the intensity of a spot to be negligible, for they are very strongly absorbed by the crystal.

The intensity of reflexion from a certain plane as measured from the density (blackening) of the Laue spots cannot always be taken proportional to the energy of the reflected rays. Wyckoff ‡ has carefully calculated the effect of the general radiation from a Coolidge tube with a tungsten target for different maximum voltages. His curve for 60 K.V. shows that the blackening effect of wave-lengths longer than  $5$  Å. is approximately proportional to their relative energy. At this point the effect begins to increase, suddenly reaching a maximum at  $\lambda = 485$  Å. (critical absorption for silver); the maximum effect is maintained roughly to  $\lambda = 4$  Å.

\* Ledoux-Lebard and Dauvillier, 'La Physique des Rayons-X.'

† Hull and Rice, Proc. Acad. Nat. Sci. ii. (1916).

‡ Wyckoff, Amer. Journ. Sci. I. p. 336 (1920).

After this point the blackening effect falls very rapidly (the effect of critical absorption by bromine of  $\lambda = 917 \text{ \AA}$ . need not be considered, as energy of this wave-length is very small).

This abnormal effect on the photographic plate of certain wave-lengths affords a very convenient means of detecting the wave-lengths reflected by certain planes, for we can generally assume that the intensity of most of the strong spots produced by planes having comparatively complex indices is largely due to wave-lengths which lie between  $49 \text{ \AA}$ . and  $4 \text{ \AA}$ . for 60 K.V.

We have already found that the symmetry plane of the crystal is a glide-plane, and its basic lattice is  $\Gamma m$ ; the number of molecules per cell is therefore either 2 or 4.

Pl. XXI. shows that the spots corresponding to the rather complex planes (131), (141), and (161) are very strong, and that the spot reflected by the plane (151) is weak. The spacings of these planes corresponding to 2 and 4 molecules per cell were calculated from the corrected crystallographic data and the glancing for these planes observed. The wave-lengths reflected by each of them calculated therefrom are shown below.

TABLE V.

	131.	141.	161.	151.
$N = 4 \dots \dots \dots \left\{ \begin{array}{l} \lambda_1 = 1.31 \\ \lambda_2 = .66 \\ \lambda_3 = .44 \\ \lambda_4 = .34 \end{array} \right.$	$\lambda_1 = 1.31$	$\lambda_1 = .90$	$\lambda_1 = .49$	$\lambda_1 = .67$
	$\lambda_2 = .66$	$\lambda_2 = .45$	$\lambda_2 = .25$	$\lambda_2 = .34$
	$\lambda_3 = .44$	$\lambda_3 = .30$		
	$\lambda_4 = .34$			
$N = 2 \dots \dots \dots \left\{ \begin{array}{l} \lambda_1 = 1.05 \\ \lambda_2 = .53 \\ \lambda_3 = .35 \end{array} \right.$	$\lambda_1 = 1.05$	$\lambda_1 = .71$	$\lambda_1 = .39$	$\lambda_1 = .53$
	$\lambda_2 = .53$	$\lambda_2 = .36$		$\lambda_2 = .27$
	$\lambda_3 = .35$			

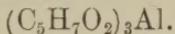
From the foregoing discussion on the intensity of Laue spots it follows that the intensity of the spots produced by all the three planes (131), (141), and (161) could not have been very strong unless each reflected a wave-length which is photographically very effective. The above table clearly

shows that this is true when N is 4, for the 3rd-, 2nd-, and 1st-order reflexions from the planes (131), (141), and (161) respectively are produced by wave-lengths all of which lie within the most effective range ( $49\text{--}4$ ) Å. On this assumption a weak spot from the plane (151) is also accounted for. On the other hand, if N had been 2, none of these spots should have been strong (possibly excepting that due to (161)). A strong spot due to (131) also proves that the basic lattice of the crystal cannot be  $\Gamma m'$ .

The reflexion from the plane  $b$  (010) does not occur on the plate; therefore the exact nature of the symmetry-axis could not be decided from the Laue photograph of the  $a$  (100) face of the crystal.

The final conclusions from the observed data are therefore that the space-group is  $C_{2h}^4$  or  $C_{2h}^5$ , according as the axis of symmetry is a simple or screw-axis, and that the molecules are asymmetric.

### (C) ALUMINIUM ACETYLACETONE.



Lang \* describes this crystal as follows :—

Class : Monoclinic prismatic.

Forms :  $a$  (100),  $m$  (110),  $c$  (001),  $g'$  (101),  $b'$  (103).

$$a:b:c = 1.901:1:1.361; \quad \beta = 98^\circ 54'.$$

Facets belonging to the forms  $g'$  (101) and  $b'$  (103) gave very poor reflexions, and he was not satisfied that they corresponded to real faces.

Subsequent examination of the crystals by T. V. Barker † showed that the form  $g'$  was actually developed and that  $a:g' = 66^\circ 26'$  (not  $62^\circ 24'$  as observed by Lang). The crystal elements according to the new observations are therefore :—

$$a:b:c = 1.901:1:1.111.$$

A Laue photograph was taken with the rays incident normally on  $c$  (001) face and the  $b$ -crystallographic axis vertical. The pattern obtained is shown in Pl. XXII. The maximum voltage through the tube was 60–70 K.V. and the distance of the plate from the crystal 4 cm.

\* v. V. Lang, *Sitzungber. d. Akad. d. Wiss. (Wien)*, cxii. (2 a), p. 1166 (1902).

† Morgan and Drew, *Trans. Chem. Soc.* cxix. (ii.), p. 1064 (1921).

The identification of one of the six pairs of spots on the vertical line through the centre of the pattern is shown in the following table. The fourth column gives the indices of the corresponding planes according to the axial ratios observed by Barker.

TABLE VI.

INT.	Obs. $\theta$ .	Calc. $\theta$ .	Indices of Planes.	Corrected Indices.
S .....	6° 20'	6° 30'	081	041
M .....	8° 21'	8° 38'	061	031
VS .....	12° 15'	12° 40'	041	021
WM.....	16° 30'	16° 50'	031	032
M.....	18° 26'	18° 50'	083	043
M.....	24° 11'	24° 30'	021	011

The table shows that spots due to the planes 071 and 051 do not occur. Since strong reflexions from more complex planes (081 and 061) are present, it is improbable that the total absence of the spots from 071 and 051 is due to these planes reflecting weakly. Furthermore, in a normal case this cannot be accounted for on the supposition that the rays reflected by them are all outside the range of wave-lengths which was used, or that they had very little photographic value, for the spacing and glancing angles for 071 are intermediate between those of 081 and 061, and therefore the wave-lengths reflected by it should have an intermediate value. The same reasoning holds good for 051. However, the spots due to these planes could be absent if the basic lattice of the crystal is the *c*-face-centred lattice  $\Gamma m'$ , which will halve the spacings of all planes  $(hkl)$  if  $(h+k)$  is odd. (Presence of a spot due to 031 might be assumed to be due to even-order reflexions from this plane.)

For further information on this point and the determination of the nature of the symmetry-plane, the indices of planes reflecting the various spots on the horizontal line through the centre of the photograph were obtained in the usual manner. The identification of the spots is shown in the following table:—

TABLE VII.

Spots on -ve side of <i>a</i> -axis.					Spots on +ve side of <i>a</i> -axis.				
INT.	Obs. $\theta.$	Calc. $\theta.$	Indices of Planes.	Correct Indices.	INT.	Obs. $\theta.$	Calc. $\theta.$	Indices of Planes.	Correct Indices.
Abs ...	—	3° 25'	801	401	VS ...	8° 21'	8° 54'	100	10
VW ...	7° 10'	7° 31'	601	301	VW ...	16° 37'	17° 38'	11.0.1	11.0.2
Abs ...	—	8° 58'	11.0.2	11.0.4	W.....	18° 12'	19° 15'	9.0.1	902
M.....	10° 25'	10° 48'	501	502	VW ...	21° 0'	22° 0'	701	702
S .....	12° 18'	12° 46'	902	904					
VS ...	14° 54'	15° 28'	401	201					
WM...	18° 7'	18° 4'	702	704					
W ...	19° 20'	19° 56'	10.0.3	503					
W ...	22° 30'	22° 47'	801	302					

The absence of reflexion from the planes 10.0.1 and 801 and 801̄, and the presence of a very weak spot corresponding to 601̄, apparently indicate the symmetry-plane being a glide-plane and its translation parallel to its own plane either  $\frac{c}{2}$  or  $(\frac{a}{2} + \frac{c}{2})$ ; but the deduction is improbable, for spots due to the planes 501, 401, 301, etc., are present, and it does not account for the absence of a spot from 701̄. Results given in the above table furthermore show that the basic lattice of the crystal cannot be the *c*-face-centred lattice  $\Gamma m'$  which seemed probable from the study of Table VI.

If we assume the ratio of  $b : c$  to be double of Barker's ratio, the anomalous nature of reflexion from the planes of the type  $(okl)$  and  $(hol)$  disappears. The indices of the planes given in Tables VI. and VII. have been re-indexed according to the corrected axial ratios ( $a : b : c = 1901 : 1 : 2.222$ ) in separate columns of the tables headed "Correct Indices."

In Table VII. we observe that, according to the corrected axial ratios, spots corresponding to planes 501, 401, 401̄, 301̄, i.e. planes  $(hol)$ , when  $l$  is odd (excepting 201̄ and 503̄), are absent, and that reflexions from more complex planes such as

$50\bar{2}$ ,  $90\bar{4}$ ,  $70\bar{4}$ , and  $30\bar{2}$ , *i.e.* planes (*hol*), when  $l$  is not odd, occur. This indicates that the plane of symmetry is a glide-plane and its translation parallel to itself is  $\frac{c}{2}$ . Spots

corresponding to the planes  $20\bar{1}$  and  $50\bar{3}$  are exceptions, but they were found to be due to even-order reflexions from these planes.

Though the results of Tables VI. and VII. suggest the improbability of the basic lattice of the crystal being  $Tm'$ , the point could be definitely settled when the number of molecules per cell is determined and the intensities of the spots produced by certain general planes ( $hkl$ ) are compared with the wave-lengths reflected by them. Accordingly, the indices of the planes reflecting the various Laue spots were calculated from a gnomonic projection made out of the Laue diagram.

It will be noticed that though the Laue diagram (Pl. XXII.) shows a two-fold symmetry about the horizontal line, the distances from the centre of the pattern of spots reflected by two corresponding planes ( $hkl$ ) and ( $h\bar{k}\bar{l}$ ) are not exactly equal. This is evidently due to the fact that the crystal face  $c(001)$  was not quite normal to the incident beam, but rotated through a small angle about the  $a$ -axis of the crystal. For example, the distances of the spots reflected by the planes  $4\bar{1}\bar{2}$  and  $41\bar{2}$  from the centre are respectively 2.10 cm. and 2.04 cm.; and we find that the spot corresponding to  $4\bar{1}\bar{2}$  is weak, whereas that due to  $41\bar{2}$  is very strong. The spacing and grating elements of these planes are the same; and since only the glancing angles for them are different, it is evident that one of the wave-lengths reflected by  $4\bar{1}\bar{2}$  should be just outside the critical point at which the blackening effect of the rays begins to fall abruptly, *i.e.* it should be just longer than  $485 \text{ \AA}$ . (the critical absorption of silver), and that the corresponding order of reflexion from  $41\bar{2}$  should be within the range of wave-lengths which is photographically very effective.

The spacing of the plane  $41\bar{2}$  (or  $4\bar{1}\bar{2}$ ) calculated from the corrected axial ratios and density =  $1.267$  is  $3.05 \text{ \AA}$ , and the glancing angles for  $4\bar{1}\bar{2}$  and  $41\bar{2}$  as calculated from the distances of the corresponding spots are  $13^\circ 50'$  and  $13^\circ 30'$  respectively. The wave-lengths producing the 1st-, 2nd-, and 3rd-order reflexions of  $41\bar{2}$  (calculated from  $n\lambda = 2d \cdot \sin \theta$ ) are  $1.46$ ,  $.73$ , and  $.488 \text{ \AA}$ , and those of  $4\bar{1}\bar{2}$  are  $1.42$ ,  $.71$ , and

475 Å. respectively. Since the 3rd-order spectrum of  $4\bar{1}2$  is produced by  $\lambda = 488$  Å., which is just beyond the critical absorption of silver, the intensity of the corresponding Laue spot is weak. A strong spot corresponding to  $4\bar{1}\bar{2}$  is also accounted for, since the 3rd-order reflexion from this plane is due to  $\lambda = 475$  Å., which is well within the range of wave-lengths producing maximum photographic effect. It is therefore concluded that the number of molecules per cell is 4.

Since the intensity of the spot due to the plane  $4\bar{1}\bar{2}$  is mostly due to the 3rd-order reflexion, the basic lattice of the crystal cannot be  $\Gamma'm$ , for each of four cases of  $\Gamma'm$  will halve the spacing of  $4\bar{1}\bar{2}$ , and in consequence the 3rd-order reflexion from this plane should have been absent.

The final conclusions from the results given by the Laue photograph of this crystal are therefore that the molecules are asymmetric and the space-group  $C_{2h}^4$  or  $C_{2h}^5$ , according as the symmetry-axis is a simple or a screw-axis.

As the reflexion from the  $b$  (010) plane does not occur on the plate, the exact nature of the symmetry-axis could not be determined from the annexed pattern (Pl. XXII.). But Mr. Astbury has kindly supplied me with some data obtained with an ionization spectrometer. He obtains the value 3.705 Å. for the spacing of the  $b$  (010) plane. The full calculated spacing of this plane corresponding to  $N = 4$  is 7.425 Å. Thus the  $b$ -spacing is halved, and therefore the axis is a screw-axis and the space-group  $C_{2h}^5$ .

In conclusion, I wish to thank Prof. A. W. Porter, F.R.S., for his direction and advice, and to express my indebtedness to Mr. J. H. Smith, M.Sc., for his many helpful suggestions.

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CX. *The Making of a Salt Haze.*  
By J. S. OWENS, M.D., A.M.I.C.E.\*

I OBSERVED recently an interesting phenomenon which, I think, might be termed the birth of a salt haze. On March 19th, 1926, on board the Booth liner 'Hildebrand,' we were off the coast of Spain, south of Cape Finisterre; it was a bright sunny morning, with a light wind from the south-east, that is off the land. A long swell

\* Communicated by the Author.

was breaking on the rocky coast and throwing up a great deal of spray where partly submerged rocks occurred. The coast itself was partly obscured by a white haze nearly up to the tops of the hills, which appeared about 400 or 500 feet high, but this was definitely denser near the sea-level. The visibility out to sea was very good. It was 9 A.M. and the sun was over the land, the sky clear of cloud except over the land. At certain places along the coast, over projecting rocks where the spray formation was very marked, the haze referred to was definitely denser than at other points; all such parts were overhung by fairly well-defined patches of haze.

While passing through the haze on the 19th I took some records with the jet dust counter \*, and a 1000 c.c. record was distinctly visible with the naked eye. Examination under the microscope showed that the record consisted practically entirely of soluble crystalline matter. When first examined the line of the record was covered with small drops, which, on warming, dried and left well-defined crystals, chiefly skeletal and fern-like, some very small and indefinite in shape. There was a star-shaped crystal of eight rays, outside diameter about 4 microns; one imperfect star with one long ray, like a dagger blade, about the same size, but the crystals were mostly skeletal.

On the following morning, farther south along the same coast, it is perhaps of significance to note that there was a dense fog which gradually cleared as the sun got up, so that it was practically gone at 9 A.M. At this time I took a wet and dry bulb observation which showed a dry bulb temperature of 54.5° F. and wet 50° F. This represents a relative humidity of 71 per cent., which is therefore a little below the humidity at which sodium chloride deliquesces †, and it seems to convey the suggestion that the presence of salt crystals in the air may have been responsible for the fog.

On several occasions, haze composed practically entirely of salt crystals has been found in the vicinity of the sea. Such hazes have already been described in the Proceedings of the Royal Society, A, ex. (1926), and in the Ninth and Tenth Annual Reports of the Advisory Committee on Atmospheric Pollution.

It seemed worth while finding, if possible, the humidity conditions under which the actual crystals obtained in the record taken on the 19th would deliquesce. The cover glass

\* Proc. Roy. Soc. A, ci. (1922).

† "Condensation of Water from the Air upon Hygroscopic Crystals," by J. S. Owens, Proc. Roy. Soc. A, ex. (1926).

with its record was therefore removed from its mounting ring and set up on three wax pellets above a glass slip, leaving about 2 mm. air-space between the record and the slip, the record being on the face of the cover glass next the slip. The crystals were observed under the microscope during different conditions of humidity as it altered naturally. The humidity was measured by an Assmann psychrometer, the bulbs of which were placed in close proximity to the record.

The first observation showed the record to consist of drops only, the humidity was then 77 per cent. It fell to 74 per cent. without any change in the drops. The next observation was at a humidity of 51 per cent., and all the drops had disappeared, leaving dry crystals; this condition persisted when the humidity rose again, and the last observation was at 64 per cent., the crystals being all dry. During the last observation, on breathing near the record the trace became immediately converted into a line of drops, which disappeared again in three or four seconds, showing the rapid response to the surrounding conditions.

The crystalline matter present in the air on the 19th was capable of collecting moisture, or retaining it, at 74 per cent. relative humidity at a temperature of 61.5° F., but lost its moisture at 64 per cent. at a temperature of 58° F. This is significantly similar to the behaviour of crystals of sea salt when observed under changing conditions of humidity.

The above observations may throw some light upon the reputation which the Spanish and Portuguese western coasts have for fogs. It is evident that if the atmosphere contains large numbers of crystals which deliquesce at humidities 25 per cent. below saturation, the conditions for fog formation must be exceptionally favourable. The nature of the coast and the exposure to the Atlantic swell is such that it must be a prolific factory for salt haze, and apparently this may easily become converted into a thick fog.

The method of formation of such a haze is worth considering. It appears probable that the origin of the haze may have some effect upon the distribution of the different salts forming it. It is well known that sea salt is a mixture consisting mainly of sodium chloride but with considerable proportions of other salts, such as magnesium chloride. If a salt haze is developed from spray thrown up from the surface of the sea under the action of the wind, the crystals resulting from the evaporation of the liquid suspended in the air will be composed of a mixture of all salts present. If we picture a drop of solution of a mixture of sodium and magnesium

chlorides drying while suspended in the air, the less hygroscopic sodium chloride will doubtless crystallize out and form a solid core to the drop when the humidity falls below about 75 per cent.; but at this stage there would be surrounding the core a more concentrated solution of magnesium chloride, and this would not evaporate until the air became much drier. Thus we might expect a core of sodium chloride with surface crystals of magnesium chloride. With such a formation it is not easy to see how a selective deposit could take place unless the surface crystals of the more hygroscopic salt became separated in some way from the less hygroscopic core.

There are, however, other ways in which it is probable the salt haze is generated, which might produce a suspension of crystals in which the different salts were separated. For example, in the case of flat sandy foreshores where a great expanse of sand is exposed at low water there is usually a marked drift of sand under the action of the wind. This is responsible for the formation of sand dunes which often border the coast near such foreshores. The wind is capable of picking up sand while the latter is wet with sea water, and the sand may often be observed drifting in a dense layer over the surface of the damp foreshore. The sand particles being wetted with sea water, under suitable conditions no doubt the surfaces of the grains become coated with minute crystals of sea salts; these crystals may be detached by the rubbing of the sand grains together under the action of the wind, and thus a haze of very fine crystalline matter be distributed in the air. Such a haze would probably have the crystals of the different salts to a great extent separated from each other, and as the humidity of the air alters there would probably be a selective settlement of the more hygroscopic particles before the others. If, for example, we picture conditions when the relative humidity is over 75 per cent. for some time and the air is still, it would seem to be probable that all the salts which deliquesce at humidities above this would tend to settle out by virtue of their increased mass after deliquescence, thus leaving behind the salts which remain dry under those conditions.

I do not think we can assume, as has been done (Kohler)\*, that salts derived from the sea necessarily maintain the same composition when suspended in the air.

\* Hilding Kohler, "The Condensation of Vapour in the Atmosphere," Geophysical Publications, vol. ii., Danish Geophysical Commission, 1921.

*Haze at Holme, Norfolk.*

The following observation was made on August 31st and September 1st, 1926, on the coast at Holme, which is situated on the southern coast of the Wash :—A strong wind was blowing in from the sea on Tuesday, August 31st; the direction was about NW'N., and on Wednesday this veered to nearly due North. The velocity was approximately 20 miles per hour, as measured by the flight of thistledown over a measured distance. The sea was rough and there was a large quantity of sand blowing on the foreshore. A dense haze covered the land, the limit of visibility being about 5 miles. The same was true over the sea, the horizon being very hazy. The weather was fine, except that on the night of Tuesday, August 31st, there was a slight fine rain.

On Wednesday, September 1st, a trap was set up with the object of catching some of the haze particles. This trap was made from a tin, about 100 millimetres diameter and 120 millimetres long, and open at one end. In the middle of the closed end of this tin a hole about 2 millimetres diameter was punched, and it was set up with the open mouth facing the wind with a microscope slide wedged about 2 millimetres behind the hole, so that the jet of air passing out through the hole in the bottom struck the microscope slide. The apparatus was set up about 100 yards landward of the foreshore. The tides at the time were neaps, and a large area of sand on the foreshore was exposed; the sand, as stated above, was drifting with the wind.

The first slide was put in at 10.30 A.M., and at 11.15 A.M. a patch visible to the naked eye had formed opposite the hole. The slide was removed at 12.30 P.M. and, examined under a low power, showed mostly drops, which disappeared on warming the slide, leaving what was apparently crystalline deposit behind. Slide No. 2 was put in at 12.30 P.M. and removed at 3.35 P.M. The haze during the whole time remained about the same. On examining these slides under the microscope on my return to London, the visible patches were seen to consist almost entirely of drops. At the time of examination the humidity was taken with an Assmann psychrometer, the wet bulb was 63.7° F., the dry 67.4° F., indicating a relative humidity of 80 per cent. On warming the slides gently the drops disappeared and crystals were formed. These were mostly skeletal crystals with arms at 90°. The crystals were allowed again to deliquesce, when a few rhomboid crystals were found which did not liquefy. On being re-warmed, a large number of well-formed squares

and rectangular plates appeared. The second slide showed the same appearance, except that there were large numbers of rhomboid crystals scattered through the drops, and, on drying, numbers of cubical crystals having sides up to 24 microns diameter became visible—evidently sodium chloride,—but there were also a number of skeletal crystals with 90° arms.

It is evident, therefore, that the haze contained, if it did not entirely consist of, large numbers of salt crystals, and as they were probably at the time partly if not completely deliquesced, it appears to be a somewhat interesting condition—probably the transition state from a haze of dry crystals to a fog of liquid drops. It is important to note that the relative humidity at which the crystals were found to have deliquesced was 80 per cent., while common salt is known to deliquesce at 74 per cent. to 75 per cent. relative humidity. The sea during the observation was rough, and doubtless one of the sources of the haze particles was the spray carried in the wind, but there was as well a large expanse of open foreshore over which sand was blowing, and this sand being wet with sea water doubtless set free salt particles into the wind. Particles so set free from blowing sand need not have the same composition as sea salt, as the selective deliquescence of the salts would come into operation, some adhering to the sand particles when wet, while others might be crystalline and free to be knocked off by the impact of the sand particles with each other.

CXI. *The General Theory of the Sensation of Flickers in Peripheral and Central Vision.* By P. LASAREFF, Member of the Academy of Sciences (Leningrad), Director of the Institute of Physics and Biophysics (Moscow) \*.

**I**N my publications from the year 1914 I have demonstrated that many phenomena observed with Flickers can be explained if we apply the ionic theory of stimulation developed by myself †.

For the moment at which we obtain a continuous sensation of illumination, the number of light interruptions in

\* Communicated by the Author.

† Article by P. Lasareff in the special publication of the Ledentzov Society in Moscow, with an English resumé, 1914; later the same theory was published in my book 'Recherches sur la théorie ionique de l'excitation' (Moscou, 1918), and in P. Lasareff, 'Ionentheorie der Reizung' (Bern und Leipzig, 1923).

a second N, the intensity of the light J, and the time t of darkness adaptation after strong illumination of the retina are connected by the following formula :

$$(N - N_0) \sqrt{4\pi^2 N^2 + \alpha_2^2} = \alpha_1 k J C_0 (1 - e^{-\alpha_3 t}) A.$$

$N_0$ ,  $\alpha_2$ ,  $\alpha_3$ ,  $C_0$ ,  $\alpha_1$ , and A are constants ; k is the constant of absorption.

The above formula may be written in another way :

$$\log(N - N_0) + \frac{1}{2} \log(4\pi^2 N^2 + \alpha_2^2) = \log J + B. . . . . (1)$$

B is a constant.

Later Allen proposed another empirical formula connecting N and J\*. This formula has the form

$$N = A \log J + B. . . . . (2)$$

A and B are constants which can be determined from experimental data.

In Allen's experiments, which confirmed excellently formula (2), the variations of N and J are very large, and it is necessary to investigate the connexion between the formulæ (1) and (2).

This question is the purpose of the present paper.

### § 1. *General Theory of the Photochemical Phenomena during periodical illumination of the retina.*

We will first investigate the influence of the periodical illumination of the layer of sensitive pigment. The concentration of this pigment is C and the concentration of the ionized products of photochemical reaction is  $C'_1$ .

As I have shown in my previous works†, the velocity of the reaction which gives the stimulating ionized products must be proportional to the absorbed energy, which is, when C is small, equal to  $\alpha_1 k J C$  (J is the periodically varying intensity of light). At the same time as the destruction of the pigment we have, in the retina, the process of restoration of sensitive pigment. As I have demonstrated, this process has a velocity  $-\alpha_2 C'_1$ . We

\* F. Allen, Phil. Mag. ser. 6, xxxviii. p. 81 (1919).

† P. Lasareff, Pflüger's Archiv, cliv. p. 459 (1913) and clv. p. 310 (1914). P. Lasareff, 'Recherches sur la théorie ionique de l'excitation,' p. 86 (Moscou, 1918). P. Lasareff, 'Ionentheorie der Reizung,' p. 13 (Bern und Leipzig, 1923).

have therefore for the process taking place in the retina during the action of light on the retina the following differential equation for the velocity of the reaction :

$$\frac{dC_1'}{dt} = \alpha_1 k J C - \alpha_2 C_1' ;$$

or putting  $J = J_0(1 - \sin nt)$ , where  $n = 2\pi N$ , we have

$$\frac{dC_1'}{dt} + \alpha_2 C_1' = \alpha_1 k J_0 C (1 - \sin nt). \dots \quad (3)$$

The oscillation of  $C$  during continuous sensation is very small and the change in  $C$ , which produces the adaptation, is very slow, and we can therefore assume that during the experiment  $C$  is constant.

With this hypothesis we obtain the solution of (3) in the form

$$C_1' = \frac{\alpha_1}{\alpha_2} k J_0 C - \frac{\alpha_1 k J_0 C}{\sqrt{\alpha_2^2 + n^2}} \cdot \sin(nt - \phi), \dots \quad (4)$$

$\tan \phi$  being equal to  $\frac{n}{\alpha_2}$ .

This equation gives us the law for the variation of concentration of the products during periodical illumination of the retina.

The amplitude of the variation of concentration is equal to

$$A = \frac{\alpha_1 k J_0 C}{\sqrt{\alpha_2^2 + n^2}}.$$

If we take into consideration that  $C$  varies very slowly in the darkness after the complete destruction of the pigment by the action of intensive light, we can calculate that this variation can be expressed by the formula \* :

$$C = C_0(1 - \gamma e^{-\alpha_3 t}),$$

$\gamma$  being a constant dependent on the intensity of the light  $J$ , which has acted on the retina (if  $J = \infty$ ,  $\gamma = 1$ ). We obtain therefore

$$A = \frac{\alpha_1 k J_0 C_0 (1 - \gamma e^{-\alpha_3 t})}{\sqrt{\alpha_2^2 + n^2}}. \dots \quad (5)$$

\* See P. Lasareff, *Pflüger's Archiv*, clv. p. 311 (1914). P. Lasareff, 'Recherches,' p. 106.

§ 2. The conditions which must be fulfilled in order to obtain a continuous sensation during interrupted illumination of the retina.

If we obtain a minimum sensation from flickers, the amplitude of variation of the concentration of ions (5) must be connected in the following way with the frequency  $n=2\pi N$ ,  $A=\phi(n)$ . We can therefore express this connexion in the form

$$A = \phi(n) = \frac{\alpha_1 k J_0 C_0 (1 - \gamma e^{-\alpha_3 t})}{\sqrt{\alpha_2^2 + n^2}}, \dots \quad (6)$$

or

$$\phi(n) \sqrt{\alpha_2^2 + n^2} = \alpha_1 k J_0 C_0 (1 - \gamma e^{-\alpha_3 t}). \dots \quad (7)$$

These formulæ (6) and (7) are the most general expressions for the conditions necessary for a continuous sensation during the action of flickering light, and every empirical formula giving a good agreement with experiment can be included in these formulæ. We will consider separately the three cases studied by myself and one case studied by F. Allen.

(1) *The first formula of Lasareff.*

If we make the simplest hypothesis about the form of  $\phi(n)$  and if we put  $\phi(n)=Rn$  ( $R$  is a constant) we obtain

$$n \sqrt{\alpha_2^2 + n^2} = \frac{\alpha_1 k J_0 C_0}{R} (1 - \gamma e^{-\alpha_3 t}) * \dots \quad (8)$$

(2) *The second formula of Lasareff.*

We can give to the function  $\phi(n)$  a more complicated form. For instance, we can put  $\phi(n)=R(n-n_1)$ ;  $n_1$  is a constant. In this case

$$(n-n_1) \sqrt{\alpha_2^2 + n^2} = \frac{\alpha_1 k J_0 C_0}{R} (1 - \gamma e^{-\alpha_3 t}). \dots \quad (8a)$$

This is the second type of equation proposed by myself.

(3) *The generalized formula of Allen.*

In order to satisfy the empirical formula of Allen we can put  $\phi(n)\sqrt{\alpha_2^2 + n^2}=Re^{pn}$ ;  $R$  and  $p$  are constants.

The formula (7) gives us

$$Re^{pn} = \alpha_1 k J_0 C_0 (1 - \gamma e^{-\alpha_3 t}).$$

\* P. Lasareff, Publication of the Ledenzov Society (*loc. cit.*).  
P. Lasareff, 'Recherches sur la théorie ionique de l'excitation' (*loc. cit.*).

This equation can be given another form :

$$\log R + pn \log e = \log J_0 + \log (1 - \gamma e^{-\alpha_3 t}) + \log \alpha_1 k C_0, \text{ or}$$

$$n = \frac{1}{p \log e} \log J_0 + \frac{1}{p \log e} \cdot \log (1 - \gamma e^{-\alpha_3 t}) + \frac{1}{p \log e} \cdot \log \alpha_1 k C_0 - \frac{1}{p \log e} \cdot \log R. \quad (9)$$

If the conditions of adaptation are not variable the formula is identical with Allen's equation.

#### (4) The third formula of Lasareff.

We can assume that the amplitude  $A = \phi(n)$  satisfies the following conditions.

$A$  increases with  $n$ , and we can assume that the relative increase of  $A$ , equal to  $\frac{dA}{A}$ , is proportional to  $dn$ . If  $p$  is a constant, we have

$$\frac{dA}{A} = pdn \quad \text{or} \quad A = Re^{pn},$$

$R$  being a constant.

Substituting this value of  $A$  in formula (7) we have

$$Re^{pn} \sqrt{\alpha_2^2 + n^2} = \alpha_1 k J_0 (1 - \gamma e^{-\alpha_3 t}). \quad \dots \quad (10)$$

This is the formula deduced by myself.

In conclusion we will show that the general equation

$$\phi(n) = \frac{\alpha_1 k J_0 C}{\sqrt{\alpha_2^2 + n^2}}. \quad \dots \quad (10\alpha)$$

can be made to give some interesting general results, without precise determination of the form of function  $\phi(n)$ . Indeed, as I have proved\*, during the continuous action of light having a constant intensity the concentration of stimulating ions  $C_1'$  is equal to

$$C_1' = \frac{\alpha_1}{\alpha_2} k J C.$$

At the threshold of stimulation  $C_1' = B$  [ $B$  is a constant], and the sensibility  $E = \frac{1}{J}$  is in this case equal to

$$E = \frac{\alpha_1 k C}{\alpha_2 B},$$

and from this we get

$$\alpha_1 k C = \alpha_2 B E.$$

\* P. Lasareff, *Pflüger's Archiv*, liv. p. 464 (1913). P. Lasareff, 'Recherches sur la théorie ionique de l'excitation,' p. 88. P. Lasareff, 'Ionentheorie der Reizung,' p. 17.

Substituting this value in the equation (10 a) we have

$$\phi(n) = \frac{BEJ_0}{\sqrt{1 + \left(\frac{n}{\alpha_2}\right)^2}},$$

or

$$\phi(n) \sqrt{1 + \left(\frac{n}{\alpha_2}\right)^2} \cdot \frac{1}{B} = EJ_0.$$

We conclude from this that if the product of sensibility E and the amplitude of intensity of interrupted light  $J_0$  is constant, the frequency of interruption giving a continuous sensation remains the same.

We can formulate the results obtained above as follows:—

(a) The first formula of Lasareff :

$$n\sqrt{\alpha_2^2 + n^2} = \frac{1}{R} \alpha_1 k J_0 C_0 (1 - \gamma e^{-\alpha_3 t}).$$

(b) The second formula of Lasareff :

$$(n - n_1)\sqrt{\alpha_2^2 + n^2} = \frac{1}{R} \alpha_1 k J_0 C_0 (1 - \gamma e^{-\alpha_3 t}).$$

(c) The generalized formula of Allen :

$$e^{pn} = \frac{1}{R} \alpha_1 k J_0 C_0 (1 - \gamma e^{-\alpha_3 t}).$$

(d) The third formula of Lasareff :

$$e^{pn}\sqrt{\alpha_2^2 + n^2} = \frac{1}{R} \alpha_1 k J_0 C_0 (1 - \gamma e^{-\alpha_3 t}).$$

If  $n_0$  is the value of  $n$  corresponding to the maximum adaptation (complete darkness adaptation), we obtain :

$$(a_1) \quad n_0\sqrt{\alpha_2^2 + n_0^2} = \frac{1}{R} \alpha_1 k J_0 C_0.$$

$$(b_1) \quad (n_0 - n_1)\sqrt{\alpha_2^2 + n_0^2} = \frac{1}{R} \alpha_1 k J_0 C_0.$$

$$(c_1) \quad e^{pn_0} = \frac{1}{R} \alpha_1 k J_0 C_0.$$

$$(d_1) \quad e^{pn_0}\sqrt{\alpha_2^2 + n_0^2} = \frac{1}{R} \alpha_1 k J_0 C_0.$$

} . . . (12)

} . . . (12 a)

Dividing (a) by (a<sub>1</sub>), (b) by (b<sub>1</sub>), (c) by (c<sub>1</sub>), and (d) by (d<sub>1</sub>), we find :

(A) (First formula of Lasareff)

$$\frac{n \sqrt{\alpha_2^2 + n^2}}{n_0 \sqrt{\alpha_2^2 + n_0^2}} = 1 - \gamma e^{-\alpha_3 t}.$$

(B) (Second formula of Lasareff)

$$\frac{(n-n_1) \sqrt{\alpha_2^2 + n^2}}{(n_0-n_1) \sqrt{\alpha_2^2 + n_0^2}} = 1 - \gamma e^{-\alpha_3 t}.$$

(C) (Generalized formula of F. Allen)

$$\frac{e^{pn}}{e^{pn_0}} = 1 - \gamma e^{-\alpha_3 t}.$$

(D) (Third formula of Lasareff)

$$\frac{e^{pn} \sqrt{\alpha_2^2 + n^2}}{e^{pn_0} \sqrt{\alpha_2^2 + n_0^2}} = 1 - \gamma e^{-\alpha_3 t}.$$

### § 3. The comparison of the theoretical formulæ with the experiments.

All the above formulæ (13) give more or less complicated functions of  $n$  which must all be equal to  $1 - \gamma e^{-\alpha_3 t}$ , expressing the curve of darkness adaptation, after the action of light. These formulæ (13) must be independent of the wave-length of the light producing the flicker. If, therefore, we find for all wave-lengths of interrupted light that the expression  $1 - \gamma e^{-\alpha_3 t}$  is equal to the particular function of  $n$  we are considering, we conclude that the theory coincides with experiment.

In order to test the formulæ (13) we may use the very precise data obtained by M. Schaternikoff \*. For this case the intensity of the light producing the light adaptation was great, and therefore  $\gamma=1$ . The results of the experiments of Schaternikoff and the theoretical formula are given in Tables I., II., III., IV. In all cases  $\alpha_2$  is equal to 9.75 †.

We see that in order to satisfy the condition (13) we must choose different values of  $\alpha_3$ , which are for  $\lambda=510.5$

\* M. Schaternikoff, *Zeitschr. f. Psychologie und Physiologie der Sinnesorg.* xxix. p. 241 (1902).

† P. Lasareff, Publication of Ledentzov Society (*loc. cit.*).

TABLE I.

	$\lambda = 589 \mu\mu.$	$\lambda = 670.8 \mu\mu.$
$t \text{ (min.)}$	$1 - e^{-a_3 t} \cdot \frac{n \sqrt{a_2^2 + n_0^2}}{n_0 \sqrt{a_2^2 + n_0^2}}$	$1 - e^{-a_3 t} \cdot \frac{n \sqrt{a_2^2 + n^2}}{n_0 \sqrt{a_2^2 + n_0^2}}$
$a_3 = 0.055$ .	$\frac{n_0}{2\pi} = 16.8$ .	$a_3 = 0.055. \quad \frac{n_0}{2\pi} = 15.6.$
5 .....	0.24	—
10 .....	0.24	0.43
15 .....	0.42	0.48
25 .....	0.56	0.64
35 .....	0.75	0.77
50 .....	0.85	0.88
70 .....	0.94	0.94
90 .....	0.99	0.99
	0.99	0.99
	0.99	1.00

and 589 equal to 0·055 and for  $\lambda=670\cdot8$  to 0·04. This first theoretical case therefore is in contradiction with experiment.

TABLE II.

	$\lambda = 510\cdot5 \mu\mu.$	$\lambda = 589 \mu\mu.$	$\lambda = 670\cdot8 \mu\mu.$
	$1 - e^{-\alpha_3 t}.$	$\frac{(n-n_1)\sqrt{\alpha_2^2+n^2}}{(n_0-n_1)\sqrt{\alpha_2^2+n_0^2}}.$	$\frac{(n-n_1)\sqrt{\alpha_2^2+n^2}}{(n_0-n_1)\sqrt{\alpha_2^2+n_0^2}}.$
$t$ (min.).	$\alpha_3=0\cdot055.$	$\frac{n_1}{2\pi}=5; \frac{n_0}{2\pi}=16\cdot8.$	$\frac{n_1}{2\pi}=3; \frac{n_0}{2\pi}=15\cdot6.$
5 .....	0·24	—	0·36
10 .....	0·42	0·42	0·46
15 .....	0·56	0·60	0·58
25 .....	0·75	0·74	0·74
35 .....	0·85	0·86	0·78
50 .....	0·94	0·92	0·91
70 .....	0·98	0·95	0·97
90 .....	0·99	0·99	0·99
			1·00

We see that in this case  $\alpha_3$  remains constant, and therefore the above formula gives us a good agreement with experiment.

TABLE III.

	$\lambda = 510\cdot5 \mu\mu.$	$\lambda = 589 \mu\mu.$	$\lambda = 670\cdot8 \mu\mu.$
	$(1 - e^{-\alpha_3 t}).$	$\frac{e^{pn}}{e^{pn_0}}.$	$\frac{e^{pn}}{e^{pn_0}}.$
$t$ (min.).	$\alpha_3=0\cdot045.$	$2\pi p=0\cdot2; \frac{n_0}{2\pi}=16\cdot7. \quad 2\pi p=0\cdot22; \frac{n_0}{2\pi}=15\cdot6. \quad 2\pi p=0\cdot48; \frac{n_0}{2\pi}=14\cdot7$	
5 .....	0·20	—	0·31
10 .....	0·36	0·35	0·39
15 .....	0·49	0·51	0·50
25 .....	0·67	0·67	0·67
35 .....	0·79	0·82	0·72
50 .....	0·90	0·91	0·88
70 .....	0·96	0·94	0·96
90 .....	0·98	1·01	0·98

TABLE IV.

	$\lambda = 510.5 \mu\mu.$	$\lambda = 589 \mu\mu.$	$\lambda = 670.8 \mu\mu.$
	$\frac{e^{pn} \sqrt{\alpha_2^2 + n^2}}{e^{pn_0} \sqrt{\alpha_2^2 + n_0^2}}$	$\frac{e^{pn} \sqrt{\alpha_2^2 + n^2}}{e^{pn_0} \sqrt{\alpha_2^2 + n_0^2}}$	$\frac{e^{pn} \sqrt{\alpha_2^2 + n^2}}{e^{pn_0} \sqrt{\alpha_2^2 + n_0^2}}$
$t$ (min.).	$\alpha_3 = 0.045$ . $2\pi p = 0.15$ ; $\frac{n_0}{2\pi} = 16.7$ .	$2\pi p = 0.15$ ; $\frac{n_0}{2\pi} = 15.6$ .	$2\pi p = 0.4$ ; $\frac{n_0}{2\pi} = 14.7$ .
5 .....	0.20	—	0.30
10 .....	0.36	0.32	0.38
15 .....	0.49	0.49	0.50
25 .....	0.67	0.66	0.67
35 .....	0.79	0.81	0.72
50 .....	0.90	0.90	0.88
70 .....	0.96	0.93	0.96
90 .....	0.98	1.01	0.98
			1.01

We see from these tables that with the formulæ

$$\frac{(n-n_1) \sqrt{\alpha_2^2 + n^2}}{(n_0-n_1) \sqrt{\alpha_2^2 + n_0^2}} = 1 - e^{-\alpha_3 t}, \quad \frac{e^{pn} \sqrt{\alpha_2^2 + n^2}}{e^{pn_0} \sqrt{\alpha_2^2 + n_0^2}} = 1 - e^{-\alpha_3 t},$$

and  $\frac{e^{pn}}{e^{pn_0}} = 1 - e^{-\alpha_3 t}$

we obtain a good agreement with the experimental results, the formula

$$\frac{n \sqrt{\alpha_2^2 + n^2}}{n_0 \sqrt{\alpha_2^2 + n_0^2}} = 1 - e^{-\alpha_3 t}$$

being in contradiction with Schaternikoff's experiments, because  $\alpha_3$  changes for different wave-lengths. We conclude from this that formulæ 12 (b, c, d) can be used to express the law of the phenomena of flickers. In order to decide which of these three formulæ (b, c, or d) expresses the actual relations, we can test the equations 12 (b and d) by comparing with Allen's experiments. The formula (12, c) is a generalization of Allen's empirical formula and for constant adaptation gives the same relation between  $n$  and  $J$  as Allen's original formula, which is in good agreement with experiment. We need therefore to test only the formulæ 12 (b) and 12 (d).

In Tables V. and VI. we give for three wave-lengths  $\lambda = 520 \mu\mu$ ,  $\lambda = 590 \mu\mu$ , and  $\lambda = 665 \mu\mu$  the values of  $J$  observed and  $J$  calculated from the formula

$$J = \sqrt{\alpha_2^2 + n^2} \cdot (n - n_1) B$$

( $B$  is a constant; Table V.), and from the formula

$$J = \sqrt{\alpha_2^2 + n^2} \cdot e^{p(n-c)} \text{ (Table VI.).}$$

TABLE V.

$$\lambda = 590 \mu\mu.$$

$\frac{n}{2\pi}$	$J$ (obs.).	$J = 0.00093 \left( \frac{n}{2\pi} - 50 \right) \sqrt{\alpha_2^2 + n^2}$
65.36	1.000	0.93
61.52	0.883	0.873
61.73	0.587	0.672
56.18	0.250	0.323
51.02	0.117	0.048
42.02	0.030	negative
33.03	0.0076	value
27.32	0.0022	of $J$ .
25.19	0.0010	
23.04	0.0007	

We see from this, that the first formula proposed by myself is in contradiction with Allen's data (fig. 1)

Fig. 1.

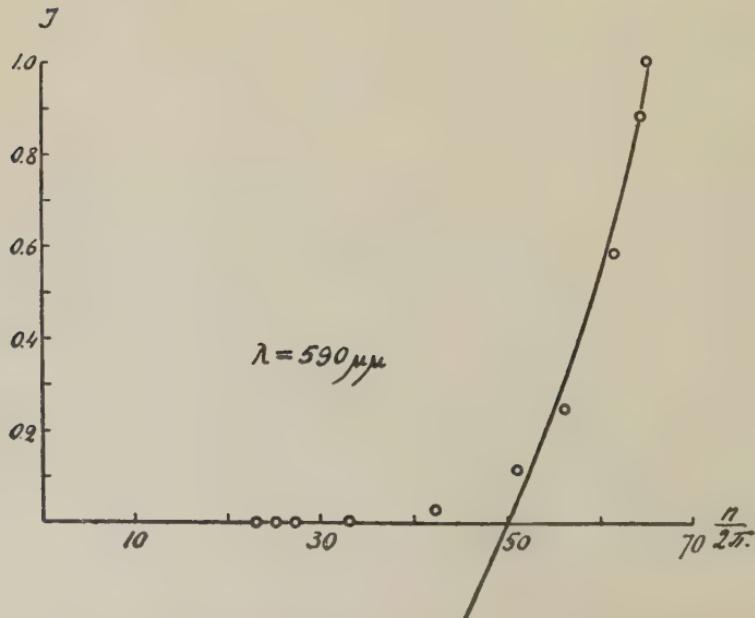


TABLE VI.

	$\lambda = 520 \mu\mu.$	$\lambda = 580 \mu\mu.$	$\lambda = 665 \mu\mu.$
	$J = \sqrt{a_2^2 + n^2} e^{p(n-c)}$	$J = \sqrt{a_2^2 + n^2} e^{p(n-c)}$	$J = \sqrt{a_2^2 + n^2} e^{p(n-c)}$
	$2\pi p = 0.1485.$	$2\pi p = 0.1306.$	$2\pi p = 0.1248.$
$\frac{n}{2\pi}.$	$J(\text{obs.})$	$J(\text{obs.})$	$J(\text{obs.})$
$\frac{c}{2\pi} = 85.0.$		$\frac{c}{2\pi} = 79.73.$	$\frac{c}{2\pi} = 85.3.$
59.17	1.000	1.276	65.36
57.55	0.883	0.974	64.52
54.39	0.587	0.574	61.73
49.50	0.250	0.254	56.18
44.64	0.117	0.111	51.02
37.31	0.030	0.031	42.02
29.41	0.0076	0.0076	33.03
24.09	0.0022	0.0028	27.32
21.41	0.0010	0.0017	25.19
23.04	0.0007	0.0014	12.19
			0.0010,
			0.0012

Fig. 2.

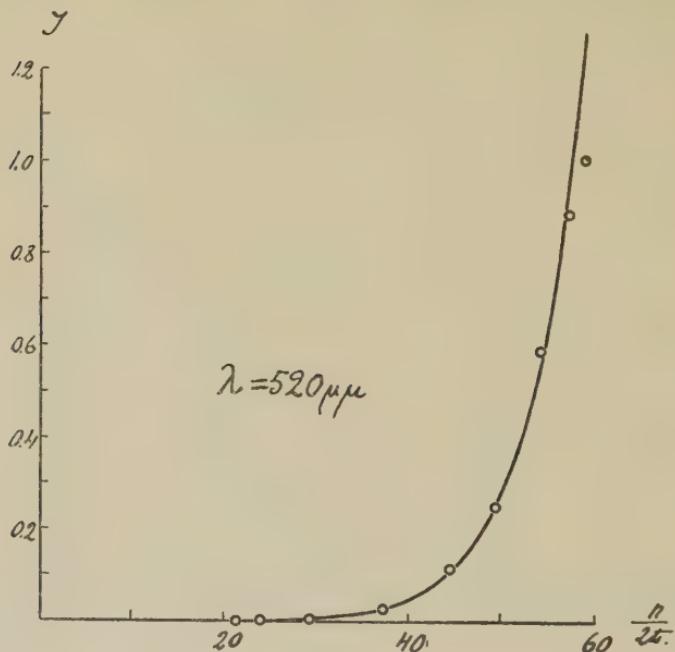
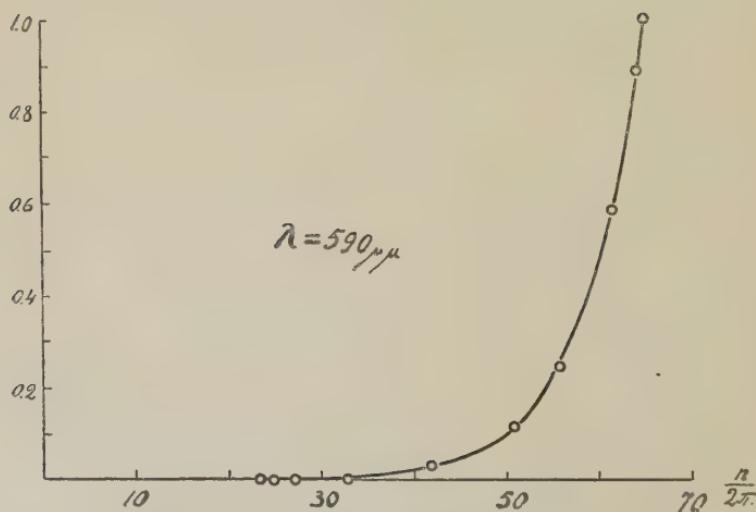


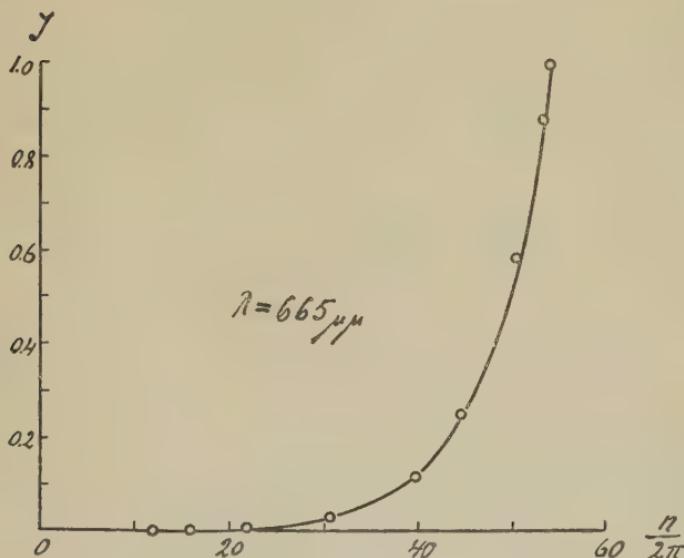
Fig. 3.



The results of Table VI. are given in figs. 2, 3, 4, which represent the relation between  $\frac{n}{2\pi}$  and  $J$  (obs.) (circles) and

$J$  calculated (continuous line), (abscissæ are  $\frac{n}{2\pi}$ ). We see that the formula (12, d) gives very good agreement with the experiments of Allen.

Fig. 4.



From what has been said above we may conclude that the formulæ determining the threshold of continuous sensation during the action of flickering light which are in best agreement with Allen's and Schaternikoff's experimental results have the form

$$e^{pn} = \frac{1}{R} \alpha_1 k J_0 C_0 (1 - \gamma e^{-\alpha_3 t})$$

and

$$e^{pn} \sqrt{\alpha_2^2 + n^2} = \frac{1}{R} \alpha_1 k J_0 C_0 (1 - \gamma e^{-\alpha_3 t}).$$

It is impossible now to decide which of these formulæ—the generalized formula of Allen or the third formula of Lasareff—is in better agreement with experiment.

The importance of the study of flickers suggests the further investigation of this region of science, and experiments with the phenomena of flickers are being pursued in my Institute.

Moscow, Institute of Physics  
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3 Miusskaja, 3.

CXII. *The Legendre Function of Order  $-\frac{1}{2}$ .*  
*By H. V. LOWRY\*.*

1. THE Legendre function of order  $-\frac{1}{2}$  is the solution of

$$(1-x^2) \frac{d^2y}{dx^2} - 2x \frac{dy}{dx} - \frac{1}{4}y = 0, \quad \dots \quad (1)$$

which equals 1 when  $x=1$ .

The solution regular near  $x=1$  satisfying this condition is

$$F\left(\frac{1}{2}, \frac{1}{2}, 1, \frac{1-x}{2}\right).$$

The general solution regular near  $x=\infty$  is

$$x^{-\frac{1}{2}}[(A + B \log x)K(x) + BI(x)], \quad \dots \quad (2)$$

where

$$K(x) = 1 + \frac{1 \cdot 3}{4^2} \frac{1}{x^2} + \frac{1 \cdot 3 \cdot 5 \cdot 7}{4^2 \cdot 8^2} \frac{1}{x^4} + \dots \dots \dots$$

and

$$I(x) = 2 \left[ \frac{1 \cdot 3}{4^2} \left( \frac{1}{3} \right) \frac{1}{x^2} + \frac{1 \cdot 3 \cdot 5 \cdot 7}{4^2 \cdot 8^2} \left( \frac{1}{3} + \frac{1}{5} + \frac{1}{7} - \frac{1}{2} \right) \frac{1}{x^4} + \dots \right].$$

$$\text{Putting } x = \frac{t^{\frac{1}{2}} + t^{-\frac{1}{2}}}{2} \text{ and } y = t^{\frac{1}{2}}w,$$

(1) becomes

$$t(1-t) \frac{d^2w}{dt^2} + (1-2t) \frac{dw}{dt} - \frac{1}{4}w = 0.$$

Hence

$$P_{-\frac{1}{2}}(x) = F\left(\frac{1}{2}, \frac{1}{2}, 1, \frac{1-x}{2}\right) = t^{\frac{1}{2}}F\left(\frac{1}{2}, \frac{1}{2}, 1, 1-t\right). \quad (3)$$

Using the analytical continuation of  $F(\frac{1}{2}, \frac{1}{2}, 1, 1-t)$ , regular near  $t=0$ , which is given in Forsyth's 'Theory of Differential Equations,' pt. 3, p. 130,

$$\begin{aligned} P_{-\frac{1}{2}}(x) &= \frac{2}{\pi} t^{\frac{1}{2}} \left[ \left( 2 \log 2 - \frac{1}{2}t \right) F\left(\frac{1}{2}, \frac{1}{2}, 1, t\right) \right. \\ &\quad \left. - \left\{ \left(\frac{1}{2}\right)^2 t + \left(\frac{1 \cdot 3}{2 \cdot 4}\right)^2 \left(1 + \frac{2}{3 \cdot 4}\right) t^2 + \left(\frac{1 \cdot 3 \cdot 5}{2 \cdot 4 \cdot 6}\right)^2 \right. \right. \\ &\quad \left. \left. \left(1 + \frac{2}{3 \cdot 4} + \frac{2}{5 \cdot 6}\right) t^3 + \dots \right\} \right]. \quad \dots \dots \dots \quad (4) \end{aligned}$$

Comparing (2) and (4) when  $t \rightarrow 0$ ,

$$A = \frac{\sqrt{2}}{\pi} (3 \log 2) \text{ and } B = \frac{\pi}{\sqrt{2}}.$$

\* Communicated by the Author.

2. The quarter period  $K$  of the Jacobian Elliptic Function of modulus  $k$  is

$$\frac{\pi}{2} F\left(\frac{1}{2}, \frac{1}{2}, 1, k^2\right) = \frac{\pi}{2k'} F\left(\frac{1}{2}, \frac{1}{2}, 1, \frac{k^2}{k^2-1}\right). \quad . \quad (5)$$

Identifying the last form in (5) with  $F\left(\frac{1}{2}, \frac{1}{2}, 1, \frac{1-x}{2}\right)$ ,

$$x = \frac{1+k^2}{1-k^2} \text{ and } t = \left(\frac{1-k}{1+k}\right)^2.$$

Hence

$$\begin{aligned} K &= \frac{\pi}{2k'} \left(\frac{1-k}{1+k}\right)^{-\frac{1}{2}} P_{-\frac{1}{2}}\left(\frac{1+k^2}{1-k^2}\right) \\ &= \frac{\pi}{2} \frac{1}{1-k} F\left(\frac{1}{2}, \frac{1}{2}, 1, \frac{4k}{(1+k)^2}\right), \end{aligned}$$

which by (4)

$$\begin{aligned} &= \frac{1}{1-k} \left[ \left( 2 \log 2 - \log\left(\frac{1-k}{1+k}\right) \right) F\left\{\frac{1}{2}, \frac{1}{2}, 1, \left(\frac{1-k^2}{1+k^2}\right)\right\} \right. \\ &\quad \left. - \left\{ \left(\frac{1}{2}\right)^2 \left(\frac{1-k}{1+k}\right)^2 + \left(\frac{1 \cdot 3}{2 \cdot 4}\right)^2 \left(1 + \frac{2}{3 \cdot 4}\right) \left(\frac{1-k}{1+k}\right)^4 + \dots \right\} \right]. \end{aligned}$$

The last form is suitable for calculating  $K$  when  $k$  is nearly 1.

By identifying each of the forms in (5) with

$$F\left(\frac{1}{2}, \frac{1}{2}, 1, \frac{1-x}{2}\right) \text{ and } F\left(\frac{1}{2}, \frac{1}{2}, 1, 1-t\right),$$

we obtain various transformations of  $K$  corresponding to the quadratic transformations of the elliptic integrals.

3. Since

$$\left. \begin{aligned} P_{-\frac{1}{2}}(x) &= F\left(\frac{1}{2}, \frac{1}{2}, 1, \frac{1-x}{2}\right) \\ P'_{-\frac{1}{2}}(x) &= -\frac{1}{8} F\left(\frac{3}{2}, \frac{3}{2}, 2, \frac{1-x}{2}\right) \end{aligned} \right\}. \quad . \quad (6)$$

Differentiating (1), we find  $P'_{-\frac{1}{2}}(x)$  satisfies

$$(1-x^2) \frac{d^2y}{dx^2} - 4x \frac{dy}{dx} - \frac{9}{4}y = 0 \quad . \quad . \quad (7)$$

Putting  $x = \frac{t^{\frac{1}{2}} + t^{-\frac{1}{2}}}{2}$  and  $y = t^{\frac{3}{2}}w$ ,

(6) becomes

$$t(1-t) \frac{d^2w}{dt^2} + (1-4t) \frac{dw}{dt} - \frac{9}{4}y = 0.$$

$$\text{Hence } P'_{-\frac{1}{2}}(x) = -\frac{1}{8} t^{\frac{3}{2}} F\left(\frac{3}{2}, \frac{3}{2}, 3, 1-t\right). \quad \dots \quad (8)$$

The general solution of (7) regular near  $x = \infty$  is

$$x^{-\frac{3}{2}} [(A' + B' \log x) K_1(x) + B'I_1(x)], \quad \dots \quad (9)$$

$$\text{where } K_1(x) = 1 + \frac{3 \cdot 5}{4^2} \frac{1}{x^2} + \frac{3 \cdot 5 \cdot 7 \cdot 9}{4^2 \cdot 8^2} \frac{1}{x^4} + \dots$$

$$\text{and } I_1(x) = 2 \left\{ \frac{3 \cdot 5}{4^2} \left( \frac{1}{3} + \frac{1}{5} - \frac{1}{2} \right) \frac{1}{x^2} + \frac{3 \cdot 5 \cdot 7 \cdot 9}{4^2 8^2} \right. \\ \left. \left( \frac{1}{3} + \frac{1}{5} + \frac{1}{7} + \frac{1}{9} - \frac{1}{2} - \frac{1}{4} \right) \frac{1}{x^4} + \dots \right\}.$$

But when  $x$  is very large, we have from (2)

$$P'_{-\frac{1}{2}}(x) = x^{-\frac{3}{2}} \{B - \frac{1}{2}(A + B \log x)\} \text{ nearly.}$$

$$\text{Hence } A' = -\frac{A}{2} + B = -\frac{\sqrt{2}}{2\pi} (3 \log 2 - 2)$$

$$\text{and } B' = -\frac{\sqrt{2}}{\pi}.$$

The corresponding solution regular near  $t = 0$  is

$$-\frac{t^{\frac{3}{2}}}{\pi} \left[ (4 \log 2 - 4 - \log t) F\left(\frac{3}{2}, \frac{3}{2}, 1, t\right) - 4 \left\{ \left(\frac{3}{2}\right)^2 \left(\frac{1}{3} - \frac{1}{2}\right)t \right. \right. \\ \left. \left. + \frac{\left(\frac{3}{2}\right)^2 \cdot \left(\frac{5}{2}\right)^2}{2} \left(\frac{1}{3} + \frac{1}{5} - \frac{1}{2} - \frac{1}{4}\right)t^2 + \dots \right\} \right]. \quad \dots \quad (10)$$

4. The mutual inductance of two parallel circular coaxial circuits radii  $a$ ,  $A$ , and  $d$  apart is

$$M = \int_0^\pi \frac{4\pi Aa \cos \theta d\theta}{\sqrt{A^2 + a^2 + d^2 - 2Aa \cos \theta}} \\ = \int_0^\pi \frac{\pi(r_1^2 - r_2^2)}{(r_1 r_2)^{\frac{1}{2}}} \frac{\cos \theta d\theta}{\sqrt{x - (x^2 - 1)^{\frac{1}{2}} \cos \theta}},$$

where  $r_1^2 = (A + a)^2 + d^2$ ,

$$r_2^2 = (A - a)^2 + d^2,$$

and  $x = \frac{r_1^2 + r_2^2}{2r_1 r_2}$ ,  $t = \left(\frac{r_2}{r_1}\right)^2$  or  $\left(\frac{r_1}{r_2}\right)^2$ .

Hence

$$\begin{aligned} M &= -\frac{\pi(r_1^2 - r_2^2)}{(r_1 r_2)^{\frac{1}{2}}} (x^2 - 1)^{\frac{1}{2}} \frac{d}{dx} \int_0^\pi \sqrt{x - (x^2 - 1)^{\frac{1}{2}} \cos \theta} d\theta \\ &= -\frac{\pi(r_1^2 - r_2^2)^2}{2(r_1 r_2)^{\frac{3}{2}}} \frac{d}{dx} \{2\pi P_{-\frac{1}{2}}(x)\} \\ &= -\frac{\pi^2(r_1^2 - r_2^2)^2}{(r_1 r_2)^3} P'_{-\frac{1}{2}}(x). \end{aligned}$$

Using the forms of  $P'_{-\frac{1}{2}}(x)$  given in (6), (8), (9), and (10), we have

$$M = \frac{\pi^2}{8} \frac{(r_1^2 - r_2^2)^2}{(r_1 r_2)^{\frac{3}{2}}} F\left(\frac{3}{2}, \frac{3}{2}, 2, -\frac{(r_1 - r_2)^2}{4r_1 r_2}\right) \dots \quad (11)$$

$$= \frac{\pi^2}{8} \frac{(r_1^2 - r_2^2)^2}{r_1^3} F\left(\frac{3}{2}, \frac{3}{2}, 3, \frac{r_1^2 - r_2^2}{r_1^2}\right) \dots \quad (12)$$

$$= \frac{2\pi(r_1^2 - r_2^2)^2}{(r_1^2 + r_2^2)^{\frac{3}{2}}} [(3 \log 2 - 2 + \log x) K_1(x) + I_1(x)] \quad (13)$$

$$\begin{aligned} &= \frac{2\pi(r_1^2 - r_2^2)^2}{r_1^3} \left[ (4 \log 2 - 4 - \log t) F\left(\frac{3}{2}, \frac{3}{2}, 1, t\right) \right. \\ &\quad \left. - 4 \left\{ \left(\frac{3}{2}\right)^2 \left(\frac{1}{3} - \frac{1}{2}\right) t + \left(\frac{3}{2}\right)^2 \left(\frac{5}{2}\right)^2 \frac{1}{2^2} \left(\frac{1}{3} + \frac{1}{5} - \frac{1}{2} - \frac{1}{4}\right) t^2 \right. \right. \\ &\quad \left. \left. + \dots \right\} \right] \dots \quad (14) \end{aligned}$$

(12) and (14) are formulæ given by Maxwell.

By using a hypergeometric transformation, (11) becomes

$$M = \frac{\pi^2(r_1 - r_2)^2}{r_1 + r_2} F\left(\frac{3}{2}, \frac{1}{2}, 2, \left(\frac{r_1 - r_2}{r_1 + r_2}\right)^2\right), \quad \dots \quad (15)$$

another formula given by Maxwell.

*CXIII. The Thermoelectric Properties of Certain Metallic Solid Solutions.* By A. L. NORBURY, D.Sc. (University College, Swansea) \*.

CONTENTS.

1. Determination of E.M.Fs. set up at temperatures between  $-191^{\circ}$  and  $500^{\circ}$  C. by certain copper alpha solid solution alloys when coupled against copper.
2. Comparison of effects of equiatomic quantities of elements in solid solution on the thermoelectric properties of copper and certain other metals.
3. A new type of thermoelectric formula.

**1. DETERMINATION OF E.M.Fs. SET UP AT TEMPERATURES BETWEEN  $-191^{\circ}$  AND  $500^{\circ}$  C. BY CERTAIN COPPER ALPHA SOLID SOLUTIONS WHEN COUPLED AGAINST COPPER.**

THE alloys used were in the form of wires (0·03 inch diam.). Their compositions are given in Table I. ; their preparation etc. is described in previous papers † ; they were annealed at a red heat by passing them through a bunsen burner.

The E.M.Fs. set up by these alloys at various temperatures against a H.C. copper wire (0·03 inch diameter, 101·6 per cent. conductivity) were measured with a Tinsley Vernier Potentiometer reading to 1 microvolt.

The cold junctions were maintained throughout at  $16^{\circ}$  C. in a thermos flask. The hot junctions were fused (using borax) for the higher temperatures ; for the lower temperatures, satisfactory junctions were made by plugging the cleaned ends of the wires into a small piece of copper tubing.

In order to obtain reliable results it was found very necessary—owing to heat conduction—to have several inches of the couple immersed in a constant-temperature medium.

This was effected by placing the hot junctions of the couples in glass tubes—closed at one end—which were immersed to a depth of about nine inches in the vapours generated by boiling ethyl alcohol ( $78^{\circ}$ ), water ( $100^{\circ}$ ), aniline ( $183^{\circ}$ ), and napthalene ( $218^{\circ}$  C.) in 5-litre flasks, and by boiling mercury ( $356^{\circ}$ ) and sulphur ‡ ( $444^{\circ}$  C.)

\* Communicated by the Author.

† 'Journal of the Institute of Metals,' xxix. p. 423 (1923); xxxiii. p. 91 (1925)

‡ The temperature of the glass tubes in this thermostat was constant at  $438^{\circ}$  vice  $444^{\circ}$ . The difference was probably due to liquid sulphur condensing and running down the tubes.

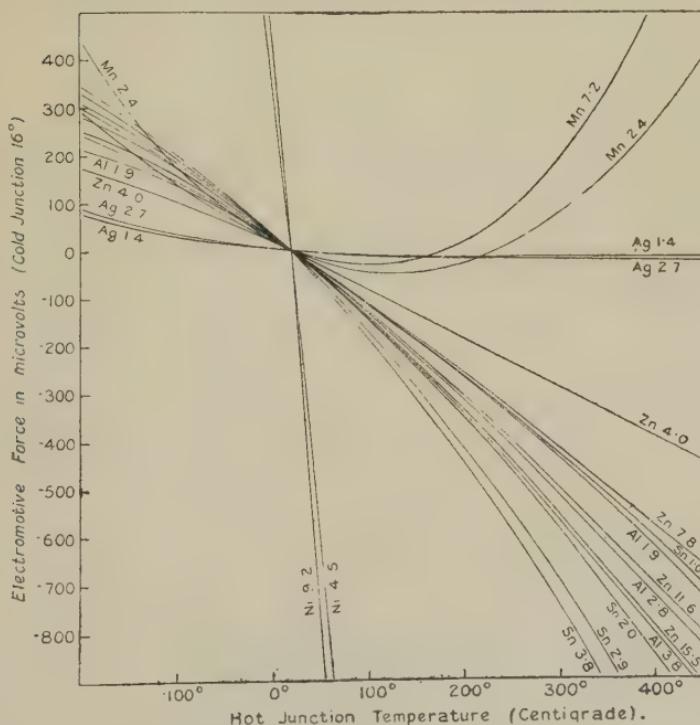
(the latter in an atmosphere of nitrogen) in four-inch internal diameter steel tubes.

For the temperatures below  $0^{\circ}\text{C}$ ., Dewar flasks containing liquid air ( $-191^{\circ}$ ), and alcohol cooled with solid carbon dioxide ( $0^{\circ}$  to  $-78^{\circ}$ ) were used. In the latter range, the temperatures were taken with a pentane thermometer, calibrated in liquid air (assumed to be  $-191^{\circ}$ ), solid carbon dioxide ( $-78^{\circ}$ ), and ice ( $0^{\circ}\text{C}$ .). For temperatures above  $444^{\circ}$  the hot junctions were placed in silica tubes immersed to a depth of about nine inches in an electrically heated bath of molten lead.

Every time an E.M.F. measurement was made, the temperature of the thermostat in question was checked by means of a calibrated Pt-Pt, Rh thermocouple, which was placed in the thermostat in a similar tube to that containing the couple under measurement.

Fig. 1.

E.M.F.s. set up against Copper by Certain Copper Alpha Solid Solution Alloys.



The E.M.F.s. set up by the various copper alpha solid solutions when coupled against copper at temperatures between  $-191^{\circ}$  and  $500^{\circ}\text{C}$ . are given in Table I, and plotted in fig. 1.

TABLE I.

E.M.F.s. set up against Copper at Temperatures between  $-200^{\circ}$  and  $500^{\circ}$ C. by Certain Copper Alpha Solid Solution Alloys.

ADDED ELEMENT.	Weight %.	ELECTROMOTIVE FORCE (microvolts) AGAINST COPPER (Cold Junction $16^{\circ}$ C.)													
		(-200°).	-191°.	(-100°).	(0°).	78°.	100°.	183°.	(200°).	218°.	(300°).	356°.	(400°).	438°.	(500°).
Al 1.92	Al 4.39	217	210	132	20	-86	-116	-	-271	-300	-442	-547	-629	-703	-827
Al 2.88	Al 6.52	315	304	184	30	-108	-144	-	-319	-354	-517	-637	-730	-809	-943
Al 3.82	Al 8.53	346	333	201	32	-117	-163	-	-355	-393	-574	-703	-805	-892	-943
Mn 2.40	Mn 2.77	443	409	174	19	-43	-50	-28	-25	-11	83	170	273	368	-
Mn 7.20	Mn 8.25	288	271	139	13	-25	-25	-	20	39	198	363	632	701	-
Ni 4.52	Ni 4.88	2580	2515	-1720	300	-1209	-1664	-3590	-4120	-4589	-6870	-8539	-9920	-11148	-
Ni 9.20	Ni 9.89	3210	3124	2100	390	-1512	-2101	-4639	-5230	-5576	-8710	-	-12954	-14833	-
Zn 4.06	Zn 3.96	175	168	100	14	-60	-84	-	-186	-206	-289	-345	-393	-433	-500
Zn 7.86	Zn 7.66	221	214	135	20	-88	-118	-	-261	-289	-415	-510	-585	-646	-753
Zn 11.66	Zn 11.36	256	248	155	24	-103	-138	-	-311	-348	-502	-615	-704	-784	-906
Zn 15.58	Zn 15.19	284	275	174	26	-108	-176	-	-341	-379	-562	-695	-794	-881	-
Ag 1.44	Ag 0.85	73	65	25	2	-6	-7	-	-14	-17	-18	-19	-19	-20	-20
Ag 2.75	Ag 1.64	88	80	30	3	-7	-8	-	-16	-19	-20	-21	-21	-22	-22
Sn 1.00	Sn 0.54	244	235	145	24	-88	-118	-244	-269	-299	-431	-531	-610	-680	-794
Sn 2.03	Sn 1.10	301	289	177	29	-115	-157	-322	-358	-392	-596	-738	-864	-956	-
Sn 2.96	Sn 1.60	334	321	192	30	-129	-178	-378	-419	-465	-701	-882	-1030	-1173	-
Sn 3.88	Sn 2.11	348	321	201	32	-138	-191	-407	-457	-503	-756	-945	-1100	-1235	-

(The E.M.F. values below the temperatures shown in brackets have been estimated by interpolation.)

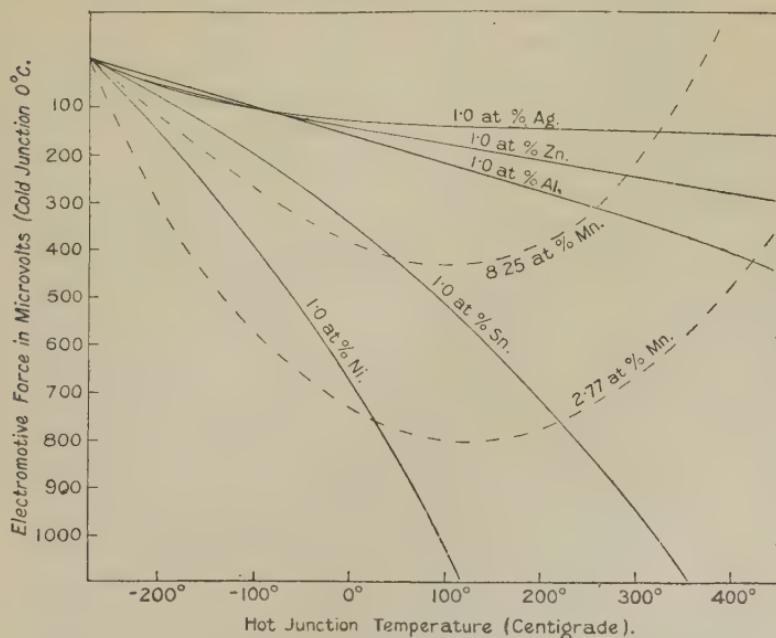
It will be seen in fig. 1 that the curves for most of the alloys are relatively simple and similar in nature. Those for the manganese-copper alloys are, however, of a different type from any of the others. The fact that manganese-copper alloys give small E.M.Fs. against copper round about room temperatures is clearly shown.

## 2. COMPARISON OF EFFECTS OF EQUIATOMIC QUANTITIES OF ELEMENTS IN SOLID SOLUTION ON THE THERMOELECTRIC PROPERTIES OF CERTAIN METALS.

In order to compare the atomic effect of one solute element with the atomic effect of another solute element

Fig. 2.

E.M.Fs. (calculated) that Copper Solid Solutions (each containing 1·0 atomic per cent. Added Element) would set up against Copper at various Temperatures if the Cold Junction was at  $-273^{\circ}$  C.



on the thermoelectric properties of copper, the curves in fig. 2 have been constructed by interpolation.

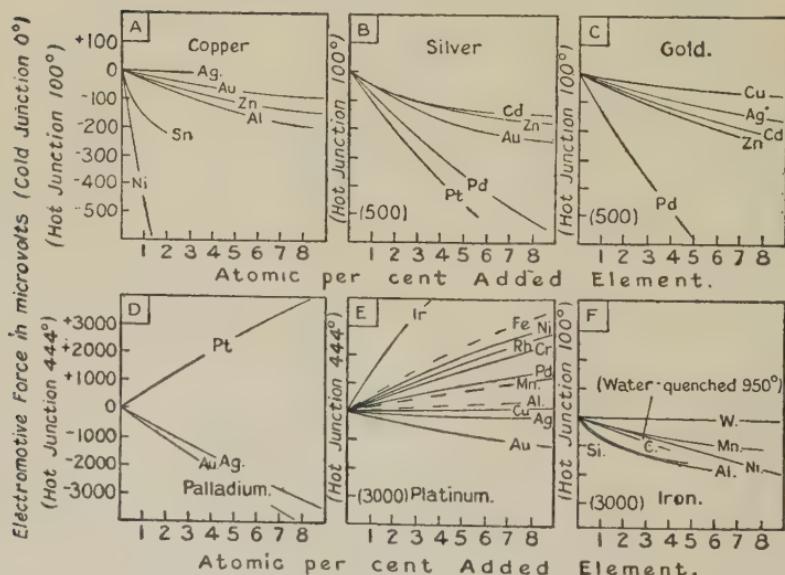
They show the E.M.Fs. that would be set up if copper alloys—each containing 1·0 atomic per cent. added element

in solid solution—were coupled against copper at the temperatures indicated. A second simplification has been introduced by constructing the curves for a cold junction temperature of  $-273^{\circ}$ , the necessary data being obtained by extrapolation. It has not been possible to construct a 1.0 atomic per cent. curve for manganese owing to this element's complicated effect. The curves for the two manganese alloys available have, however, been dotted-in in fig. 2.

Fig. 3.

E.M.Fs. set up by :—

A. Copper	Solid Solutions against Copper at $100^{\circ}\text{C}$ .
B. Silver	" " " Silver " "
C. Gold	" " " Gold " "
D. Palladium	" " " Palladium at $444^{\circ}\text{C}$ .
E. Platinum	" " " Platinum " "
F. Iron	" " " Iron at $100^{\circ}\text{C}$ . "



It is suggestive that the order of the atomic effects in fig. 1,—viz. Ag, Zn, Al, Sn, Ni,—is the same as the order of these elements in the Periodic Table, reading from Ag in Group 1 to Ni in Group 8.

In order to find out if this type of relationship occurs in other solid solutions, the curves in figs. 3 (A-F) and 4

have been constructed from the data published by previous investigators\*.

Owing to the nature of the data available it has only been possible to plot E M.F. against atomic per cent. added element for a single temperature in each case; but a study of figures 1 and 2 indicates that this should give—except in exceptional cases like the manganese-copper alloys—a general idea of the relative atomic effects of the solute elements.

In figs. 3 A, 3 B, and 3 C it will be seen that the silver and gold solid solutions are similar to the copper solid in that the solute elements in Groups 1 and 2 have small electronegative effects and those in Group 8 large electro-negative effects.

Considering now the palladium and platinum solid solutions in figs. 3 D and 3 E, it will be seen that Cu, Ag, and Au (Group 1) have electronegative effects (Cu in Pt has a small electropositive effect), while the elements in Group 8 have electropositive effects. The order of the solute elements is similar to that in figs. 3 A, 3 B, 3 C, but inverted.

Fig. 3 F shows iron solid solutions. The elements C, Mn, Ni, and W probably have complex effects in that they also cause an allotropic change to take place in the solvent metal, and the water-quenched carbon-iron alloys—although included in this figure—are not true solid solutions. The Al and Si curves should, however, be fairly representative.

The curves for the Ni solid solutions in fig. 4 have been constructed in a similar manner to those in fig. 2, only they represent 5·0 atomic per cent. alloys, since for one or two of the solute elements only one alloy of approximately this composition was tested.

It will be seen that Cu has an electronegative effect

\* These figures have been constructed from data as follows:—

- 3 A. From Table I. and from Sedström, *Annalen der Physik*, lix. (4) p. 134 (1919).
- 3 B. From Sedström, *loc. cit.*, and from Geibel, *Zeit. für Anorg. Chem.* lxix. p. 38 (1910), lxx. p. 240 (1911).
- 3 C. From Sedström and Geibel, *loc. cit.*
- 3 D. From Geibel, *loc. cit.*
- 3 E. From Geibel, *loc. cit.*, and Barus, Bull. U.S. Geol. Survey, 1889, Nos. 54 and 103.
- 3 F. From Dupuy and Portevin, Journ. Iron and Steel Inst. 1915 (1) p. 306.
4. From Robin, *Zeit. für Metallkunde*, Aug. 1924, p. 297, and from 'The Measurement of High Temperatures,' by Le Chatelier and Burgess, 1912, p. 171.

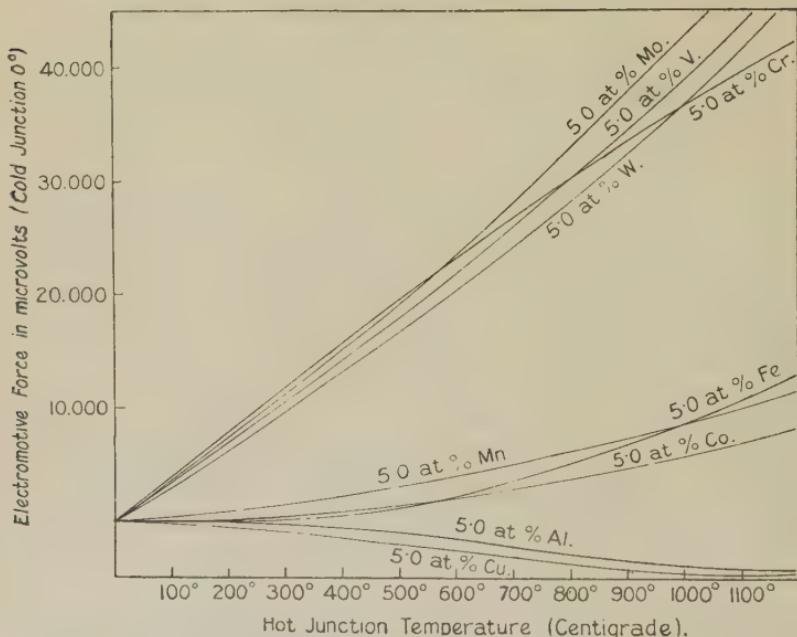
recalling the effects of Ag and Au on Pd and Pt in figs. 3 D and 3 E (since Ni, Pd, and Pt are all in Group 8 c).

The curves for several of the other solute elements in fig. 4 are somewhat complicated and cross one another.

In general, a consideration of the foregoing figures suggests that there is a connexion—provided complications do not occur—between the effect of a solute element on the thermoelectric properties of a metallic solvent and the positions of the solute and solvent elements in the Periodic Table.

Fig. 4.

E.M.F.s. set up against Nickel by Nickel Alpha Solid Solutions (each containing 5·0 atomic per cent. Added Element) at Temperatures between 0° and 1200°.



The positions of the elements in the Periodic Table necessarily only give an approximate guide to the actual factors concerned, which are presumably connected with the effects of the solute atoms on the electrons of the solvent atoms. It is significant that the effect of a solute element on the thermoelectric properties of a metallic solvent is different from its effect on the latter's electrical resistivity \*, since, in the latter case, proximity of solute and solvent in the Periodic Table—rather than position—appears to be the deciding factor.

\* Cf. Norbury, Trans. Faraday Soc. xvii. p. 251 (1921), and Journ. Inst. Metals, xxxiii. p. 91 (1925).

## 3. A NEW TYPE OF THERMOELECTRIC FORMULA.

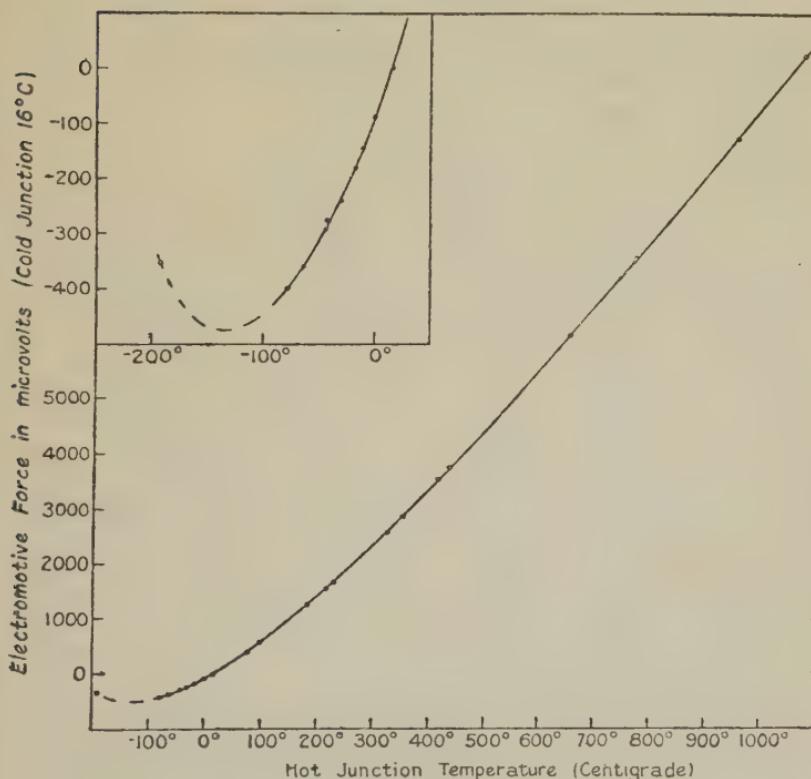
Various formulæ have been put forward from time to time for expressing the temperature-E.M.F. relationship of the platinum-platinum 90 per cent., rhodium 10 per cent. thermocouple.

The following formulæ are given by Le Chatelier and Burgess\*, who discuss and compare them :—

1.  $\sum_0^t e = mt^n$  (Holman).
2.  $\sum_0^t e = -a + bt + ct^2$  (Holborn and Day).
3.  $e = aT + b \log T + c$  (Stansfield).
4.  $t = a + be - ce^2$ .

Fig. 5.

E.M.F.s set up at Temperatures between  $-191^\circ$  and  $1083^\circ$  C. by Platinum-Platinum 90 %, Rhodium 10 % Thermocouple.



The data obtained for the Pt-Pt, Rh thermocouple used in the present experiments have been plotted in fig. 5.

\* 'The Measurement of High Temperatures,' by Le Chatelier and Burgess, p. 114 (1912).

TABLE II.

Observed E.M.Fs. of Pt—Pt 90 %, Rh 10 % Thermocouple compared with E.M.Fs. calculated using Formulae of the type: E.M.F. =  $-a + bT + c \cdot 10^{-dT}$ .

1.	2.	3.	4.	5.	6.	7.
Hot Junction Temperature. (Cold Junction, 16° C.)	E.M.F. observed. (microvolts.)	E.M.F. calculated. (Formula a.) <sup>1</sup>	Difference <sup>3</sup> . (Column 3 — Column 4.)	E.M.F. calculated. (Formula b.) <sup>2</sup>	Difference <sup>3</sup> . (Column 3 — Column 6.)	
Cent.	Abs.					
- 191	82	-356	-357	1	-383	27
- 78	195	-401	-393	- 8	-389	-12
- 62	211	-360	-345	-15	-342	-18
- 42	231	-292	-278	-14	-272	-20
- 29	244	-240	-227	-13	-217	-23
- 16	257	-181	-170	-11	-159	-22
- 10	263	-144	-142	-2	-132	-12
0	273	- 89	- 93	4	- 81	- 8
16	289	0	- 10	10	1	- 1
78	351	404	378	26	391	13
100	373	558	536	22	548	10
183	456	1234	1209	25	1216	18
218	491	1533	1523	10	1526	7
232	505	1650	1648	2	1654	- 4
327	600	2585	2583	2	2573	12
556	629	2874	2882	- 8	2868	6
419	692	3520	3550	-30	3527	- 7
438	711	3733	3755	-22	3729	4
658	931	6150	6232	-82	6167	-17
779	1052	7580	7650	-70	7553	27
961	1234	9750	9789	-49	9666	84
1083	1356	11240	11243	- 3	11094	146

<sup>1</sup> Formula a: E.M.F. =  $-5,050 + 12.0T + 5,210 \times 10^{-0.0018T}$  microvolts.

<sup>2</sup> Formula b: E.M.F. =  $-4,900 + 11.8T + 5,020 \times 10^{-0.0018T}$  microvolts.

<sup>3</sup> A difference of 1° C. causes a difference of 6 microvolts at 16° C. and 12 microvolts at 1000° C.

It will be seen that the curve passes through a minimum at about  $-135^{\circ}\text{C}$ . It follows, in consequence, that none of the above formulæ is of the right type to fit the curve at temperatures below  $-135^{\circ}$ . A formula of the following type has been found to express the results closely over a wide temperature range :

$$5. \quad e = -a + bT + c \cdot 10^{-dT},$$

where  $T$  = absolute temperature of hot junction, and  $a$ ,  $b$ ,  $c$ , and  $d$  are constants depending on the thermocouple and on the cold junction temperature. The constants can be evaluated graphically by drawing a tangent to the high temperature end of the curve and plotting the logarithms of the E.M.F. differences between the tangent and the curve against the absolute temperatures. The latter relationship, being a linear one, gives the values of the constants  $c$  and  $d$ .

The observed E.M.F. values plotted in fig. 5 are given in Table II. column 3. Columns 4 and 6 in this table show the E.M.F.s. calculated, using formulæ of the new type (5) with slightly different values for the constants in each case.

TABLE III.  
Comparison of Thermoelectric Formulae.  
(Pt-90% Pt, 10% Rh.)

Formulae 1 to 4 from Le Chatelier and Burgess, *loc. cit.*  
Formula 5 : E.M.F. =  $-8,000 + 13\cdot0T + 6,060 \times 10^{-0\cdot0018T}$ .

Substance.	Freezing Point. $^{\circ}\text{C}.$	E.M.F. observed. (microvolts.)	Observed Minus Calculated Temperature. Formula used.				
			1.	2.	3.	4.	5.
Cadmium .....	320·0	2,502	-0·2	-0·3	6·9	-1·1	-0·1
Zinc .....	418·2*	3,429	0·0*	0·0*	0·0*	0·0*	-2·5*
Antimony .....	629·2	5,529	2·3	0·0	0·0	-0·1	-1·7
Silver.....	960·0	9,111	2·5	0·2	2·2	-0·9	1·9
Gold .....	1062·5	10,296	0·4	0·2	0·0	0·0	1·3
Copper .....	1082·6	10,535	0·0	0·0	0·0	0·1	1·0
Diopside .....	1391	14,231	-6	10	-10	19	-0·6
Nickel .....	1452	14,969	-6	14	-11	28	-0·3
Cobalt .....	1490	15,423	-7	14	-13	31	0·6
Palladium .....	1549	16,140	-5	20	-14	42	1·2
Platinum .....	1755	18,613	1	42	-15	73	80

\* The F.P. of Zn is now usually taken as  $419^{\circ}\text{4 C}$ . This alters the differences in columns 1-5 to  $1^{\circ}\cdot2$ ,  $1^{\circ}\cdot2$ ,  $1^{\circ}\cdot2$ ,  $1^{\circ}\cdot2$ , and  $-1^{\circ}\cdot3$ .

Columns 5 and 7 show the differences between observed and calculated values. It will be seen that the formulæ fit the results fairly accurately, since a difference of only  $1^{\circ}$  C. causes a difference of about 6 microvolts at  $16^{\circ}$  C. and about 12 microvolts at  $1000^{\circ}$  C. There are, however, certain small systematic differences which show that the formulæ are not exact.

Columns 1–7 in Table III. are reproduced from Le Chatelier and Burgess. In this table they compare the accuracy with which formulæ 1 to 4 (referred to previously) fit the experimental results of Day and Sosman. In column 8 are shown results calculated using the new type of formula. It will be seen that this formula fits the results more accurately than formulæ 1–4,—in fact, does so within the limits of experimental error. This type of formula also fits all the results plotted in fig. 1—within the limits of experimental error.

In conclusion the author wishes to acknowledge his indebtedness to Mr. R. Wilson, M.A., for suggestions with regard to the third section of the paper; to Professor C. A. Edwards, D.Sc., for facilities for carrying out the work and for his encouragement; and to the Royal Society for a Government Grant.

#### CXIV. *The Adsorption of Nitrogen at Low Pressures by Activated Charcoal.* By RUFUS CHAPLIN, B.Sc., A.I.C.\*

##### INTRODUCTION.

THIS investigation was suggested by a consideration of the results of a preliminary study of the action of activated charcoal at ordinary temperature on traces of air. The preliminary study, undertaken in connexion with another investigation on charcoal involving vacuum technique, indicated that the nitrogen of the air is not very efficiently dealt with in a "clean-up" process carried out with a moderate amount of charcoal at ordinary temperatures. The extent to which pure nitrogen at low pressures was taken up by charcoal was therefore studied.

The experiment with nitrogen consisted in determining the  $25^{\circ}$  isotherm in the pressure region  $2 \times 10^{-4}$  to  $1.3 \times 10^{-2}$  mm. of Hg.

The preliminary experiments with air are also included in this paper and are described later.

\* Communicated by the Author.

## EXPERIMENTAL.

The pressures were measured on a modified form of McLeod gauge. The quantities of gas adsorbed are minute at these low pressures and had to be arrived at from a consideration of pressure changes in an apparatus of constant volume and sufficiently constant temperature, a special precaution being taken in the case of the isotherm to prevent the quantity errors from becoming cumulative (*vide* nitrogen experiments). Thus no other measurements but those of pressure were necessary, and since on these the validity of the results entirely depended, a specially designed McLeod gauge \* was employed. This is described in some detail below.

Fig. 1.

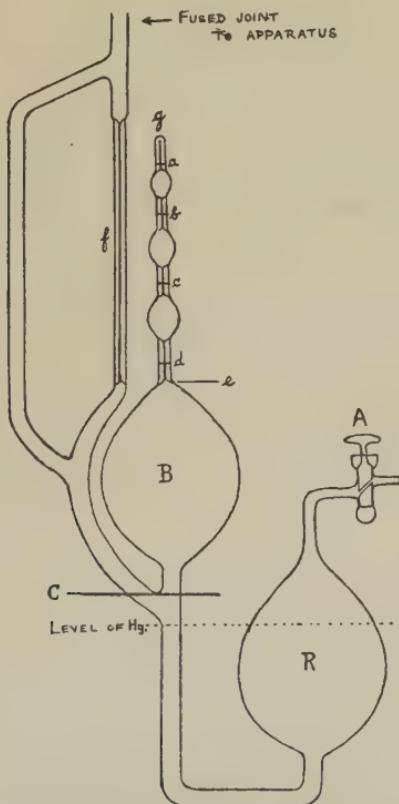


Fig. 1 shows a sketch of the gauge, which is of fused glass throughout. "R," the reservoir bulb, has a capacity of 300½ c.c. and is furnished with a vacuum tap A.

\* Due in great part to one of the author's colleagues.

The total capacity of B, including the bulbous appendix "g" to the cut-off level C, is 247 c.c.

"g" and "f" are cut from the same piece of 0·8 mm. capillary tubing, carefully selected for uniformity of bore.

"f" is 26 cm. long, "g" is 22 cm. long, and before fusing on at "e" bulbs, conveniently spaced, are blown on it as follows :—

upper bulb	0·1 c.c. capacity	}
centre	0·5 c.c.      "	
lower	1·8 c.c.      "	

(approx.).

"a," "b," "c," "d" are fine scratches on the capillary. The volumes from tip of "g" to these scratches are accurately obtained by calibration with mercury, as is also the volume per unit length of capillary round about each scratch. "g" is then fused on to "B" at "e." The sketch shows disposition of "B" and "R."

In use "B" and "R" are evacuated alternately in stages, "B" via the apparatus by the h.v. pumps, and "R" via "A" by a Geryk hand pump. To raise the Hg in "B" a sufficient pressure of air is slowly admitted through "A" into "R." "R" is evacuated again when the mercury is to be lowered. In making a measurement the mercury is slowly raised up into "g," always being brought to rest in one of the capillaries. "f" and "g" are gently tapped, and the difference in height of the two mercury columns is read off on a cathetometer to within 0·05 mm. The distance between the mercury meniscus in "g" and the selected mark is similarly read off, and this measures the volume to be added to or subtracted from the datum volume. The pressure and volume of compressed gas are thus accurately determined.

A gauge of these dimensions used in this manner for pure nitrogen gives consistent results over the range  $1 \times 10^{-4}$  to  $2 \times 10^{-1}$  mm. of Hg with an error not exceeding  $4 \times 10^{-5}$  mm. Qualitative indications of much smaller pressures can be obtained. With air the results are less consistent.

In addition to the gauge the apparatus comprised a 500 c.c. flask as further reservoir space for the gas, and a detachable silica container for the charcoal. The latter was furnished with a mercury-sealed vacuum tap and a side tube ground to fit into a ground cup fused to the apparatus, to which it was sealed with vacuum wax after the "furnacing" of the charcoal had been carried out. All other connexions

were of fused glass. The whole apparatus could be put into communication with high vacuum pumps.

The procedure was essentially the same for both the air and nitrogen experiments. The charcoal vessel being attached, the whole apparatus is evacuated to  $< 1 \times 10^{-5}$  mm. Hg, and maintained at this for several hours. No appreciable pressure must accumulate during 30 minutes of "rest." The charcoal being shut off, the gas is admitted to the main apparatus and its pressure adjusted to or near the required value\*. Time is allowed for equalization of the pressure throughout the apparatus, after which this initial pressure is read. This is corrected for the expansion which takes place into the free space over the charcoal when the latter is opened up by means of the vacuum tap to the rest of the apparatus. After a sufficient time of contact between gas and charcoal the final pressure is read, and this is the equilibrium pressure for a quantity of gas adsorbed which is simply related to the pressure change. Thus we obtain data for a point on the curve. Different points are obtained from different initial pressures. The quantity of gas adsorbed for any final pressure is obtained, in the case of air, by adding together all preceding pressure changes. Large errors were found to be introduced in this way †, and because of this and of the fact that the McLeod gauge does not give consistent results with air, the air results are not regarded as much more than semi-quantitative. In the more exact measurements on nitrogen the charcoal was evacuated (at 25° C. with the pumps) between each two points, so that only two pressure measurements were involved in the calculation of any quantity value. For purposes of comparison quantities of gas are referred to one gram of charcoal in all cases. The charcoal bulb was maintained at 25° C.  $\pm 0.05$ . The rest of the apparatus was at 17° C.  $\pm 2$ .

#### *The Results with Air.*

Three different charcoals, each evacuated for four hours at 800° C., were employed. The cooled charcoals were re-evacuated at 25° C. until they ceased to evolve a measurable pressure of gas in a period of 18–24 hours. The air used in the experiments was drawn from the atmosphere through soda-lime, calcium chloride, and finally phosphorus pentoxide, into the apparatus. The results obtained are given in

\* By operating a tap leading to the pumps.

† Evident from the trial experiments with N<sub>2</sub>—especially on desorbing—due only to accumulated errors in pressure readings.

the following Tables, in which  $P_i$  represents the initial pressure,  $P_f$  the final equilibrium pressure, and  $P_c$  the fall in pressure due to adsorption. A period of 30 minutes was allowed for equilibrium for all points.

*Results with Air at 25° C. (pressures in mm. of Hg).*

TABLE I.

Birchwood Charcoal (1.765 grams).

$P_i$	$P_f$	$P_c$	$\Sigma P_c \div 1.765$
$7.7 \times 10^{-5}$	$4.9 \times 10^{-5}$	$2.8 \times 10^{-5}$	$2.8 \times 10^{-5}$
22.8 "	15.0 "	7.8 "	10.6 "
24.0 "	19.0 "	5.0 "	15.6 "
31.3 "	23.0 "	8.3 "	23.9 "
37.5 "	25.2 "	12.3 "	36.2 "

TABLE II.

HCl extracted Birchwood Charcoal (1.783 grams).

$P_i$	$P_f$	$P_c$	$\Sigma P_c \div 1.783$
$3.3 \times 10^{-5}$	$2.3 \times 10^{-5}$	$1.0 \times 10^{-5}$	$1.0 \times 10^{-5}$
25.6 "	2.7 ? "	22.9 "	23.9 "
193.0 "	147.0 "	46.0 "	69.9 "
203.0 "	152.0 "	50.5 "	120.4 "

TABLE III.

Coconut Charcoal (4.077 grams).

$P_i$	$P_f$	$P_c$	$\Sigma P_c \div 4.077$
$5.6 \times 10^{-5}$	$3.7 \times 10^{-5}$	$1.9 \times 10^{-5}$	$1.9 \times 10^{-5}$
38.5 "	17.8 "	20.7 "	22.6 "
44.8 "	31.0 "	13.8 "	36.4 "
41.5 "	30.2 "	11.3 "	47.7 "
52.5 "	37.5 "	15.0 "	62.7 "
49.4 "	35.2 "	14.2 "	76.9 "
205.0 "	143.0 "	62.0 "	188.9 "

It will be noticed throughout how near  $P_f$  is to the partial pressure of nitrogen in the initial charge, *i.e.* to  $\frac{4}{5}$  of the initial pressure. Very little nitrogen appears to be adsorbed. In Table III. the third and fourth final pressures are practically identical, although a further considerable amount

of gas has been adsorbed in the case of point four. This is true also of points five and six. In these cases the whole of the pressure fall is due to adsorption of oxygen. If the final pressures are due practically entirely to nitrogen the non-adsorption of nitrogen in the case of points four and six would be expected, for here the initial pressures of nitrogen barely exceed the final pressures (due to nitrogen) of points preceding. The oxygen equilibrium pressures, on the other hand, are considered to be very low, in view of Lowry and Hulett's results \*, where it is shown that such quantities of oxygen as are here adsorbed are not recoverable at ordinary temperatures, *i. e.* the equilibrium pressure is very low. That the total amount of nitrogen adsorbed was small and the oxygen not recoverable was fully confirmed by opening up the charcoal to the evacuated apparatus at the end of each run. In no case was more than a trace of gas evolved.

The importance, from the present point of view, of determinations with pure nitrogen is apparent from these results with air.

### *The Results with Nitrogen.*

The preceding results indicate that the amounts of nitrogen adsorbed at these low pressures are exceedingly small, and consequently that any direct measurements must be carried out on very pure nitrogen. A trial run on atmospheric nitrogen from a cylinder showed that the impurities present masked the results entirely, causing irregularity and very marked hysteresis. Only with pure chemical nitrogen could consistent results be obtained. This nitrogen was obtained by the hypochlorite-urea reaction and purified by passage in order through dilute sulphuric acid, over heated copper gauze, soda-lime and phosphorus pentoxide. It was stored over the latter reagent.

The nitrogen pressures were read in duplicate and mean values used.

All points, with the exception of three referred to later, were determined from zero, *i. e.* on the charcoal freshly evacuated at 25° C.

The volume of the apparatus, determined by expanding nitrogen from the gauge, was 787 c.c. The free space over the charcoal in the container was estimated at 11·35 c.c. The pressure change due to expansion of the gas into the

\* Lowry and Hulett, J. A. C. S. xlvi. p. 1408 (1920).

free space is thus of the same order as that due to adsorption, and has accordingly been allowed for throughout.

Equilibrium between gas and charcoal was found to be rapidly attained, the same results being obtained with 10 minutes, 30 minutes, or 17 hours of contact. In one case the charcoal was evacuated rapidly from  $1 \times 10^{-2}$  mm. (nitrogen) to zero and then left for 48 hours. No measurable pressure was found to have developed at the end of this period.

Through pressure of other work the nitrogen determinations had to be confined to one charcoal, viz. steam-activated coconut charcoal evacuated for four hours at  $800^\circ\text{C}$ . (re-evacuated cold as foregoing samples). Weight of charcoal = 4.087 grams.

The results follow in Table IV.

### *Adsorption of Nitrogen at $25^\circ\text{C}$ .*

TABLE IV.

No.	Pressures in mm. of Hg.			Mgrs. N <sub>2</sub> adsorbed.	Mgrs. per gram charcoal.
	P <sub>i</sub>	P <sub>f</sub>	P <sub>c</sub>		
1 ...	$225.6 \times 10^{-5}$	$211.7 \times 10^{-5}$	$13.9 \times 10^{-5}$	$16.9 \times 10^{-5}$	$4.1 \times 10^{-5}$
2 ...	384.7	356.6	28.1	34.3	8.3
3 ...	516.4	479.7	36.7	44.7	10.9
4 ...	735.4	682.5	52.9	64.5	15.7
5 ...	988.7	915.6	73.1	89.1	21.6
6 ...	1037.5	957.0	80.5	98.2	23.9
7 ...	1232.0	1145.0	87.0	106.1	25.8
8 ...	598.3	551.1	47.2	57.5	14.0
9 ...	942.3	876.0	66.3	80.8	19.7
10 ...	314.4	293.2	21.2	25.8	6.3
11 ...	568.2	546.3	+21.9	52.5	12.8
12 ...	835.1	775.7	59.4	72.4	17.6
13 ...	44.0	93.7	-49.7	11.8	2.8
14 ...	1267.0	1174.0	93.0	113.4	27.6
15 ...	263.4	328.9	-65.5	33.5	8.1
16 ...	1354.0	1251.0	103.0	125.6	30.6
17 ...	24.0	22.7	1.3	1.6	0.4

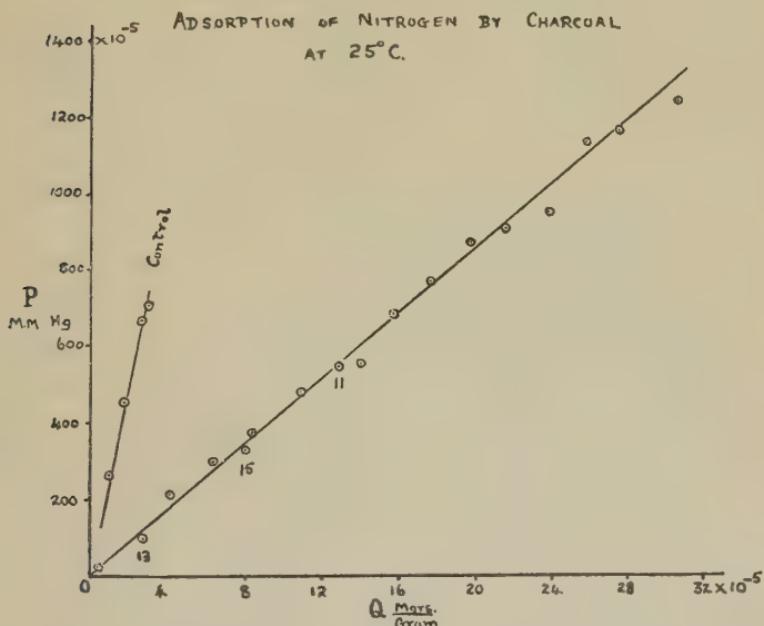
Fig. 2 shows the plot of the equilibrium pressures P<sub>f</sub> against the quantities in  $\frac{\text{mgrs.}}{\text{gram}}$ .

The only points that were not determined on the freshly evacuated charcoal were points 11, 13, and 15 (*vide* Table IV.).

Point 11 was obtained in two stages, the first stage being point 10. The pressure fall of point 11 has been added to

that of point 10 before calculating the quantity of gas adsorbed. It will be seen that point 11 lies well on the curve. This adsorption point, obtained in more than one stage, has been included to show that there is no fundamental difference in the final values whether they are arrived at in one stage or more. However, if many quantities are added in this way, a gradual accumulation of errors results, particularly evident on attempting to reverse the adsorption process\*.

Fig. 2.



Points 13 and 15 are desorption points carried out from points 12 and 14 respectively. Here the initial pressures in the apparatus were less than the equilibrium pressures over the charcoal, and consequently a rise in pressure, corresponding to a loss of gas from the charcoal, took place. These pressure changes have been subtracted from those of the preceding points, before calculating the quantity of gas remaining in the charcoal.

The weights of gas adsorbed were calculated from the pressure changes and the volume of the apparatus (787 c.c.) using the gas laws. Mean  $T=290^\circ \text{ abs}$ .

The time allowed for attainment of equilibrium in this final series of measurements was 10 minutes, which, as

\* Observed in the preliminary experiments not described here.

previously stated, was found to lead to the same results as much longer times of contact between gas and charcoal.

The points were actually determined in the order shown in Table IV.

In view of the minuteness of the quantities of nitrogen adsorbed, it was thought desirable to investigate any effect due to the interior surface of the charcoal container (silica). This was done by carrying out a few precisely similar measurements with the same container, but with the charcoal removed and replaced by the same volume of mercury. No effects beyond those due to expansion (from the apparatus reservoir into the evacuated container), as the following table shows, were found. As before stated, these were allowed for in the measurements on nitrogen and charcoal.

TABLE V.  
Control experiment without Charcoal.

$P_i$ .	$P_f$ .	$P_c$ obs.	$P_c$ calc.
$266.8 \times 10^{-5}$	$263.6 \times 10^{-5}$	$3.2 \times 10^{-5}$	$3.7 \times 10^{-5}$
461.2 „	455.6 „	5.6 „	6.4 „
711.6 „	701.6 „	10.0 „	10.0 „
680.0 „	671.0 „	9.0 „	9.5 „

Pressures in mm. of Hg.

To show the behaviour of the McLeod gauge, these observed pressure changes due to expansion were divided by the weight of charcoal, converted to mgrs. of  $N_2$ , and plotted against the final pressures in fig. 2 alongside the adsorption curve.

#### DISCUSSION.

These two curves represent exactly comparable results obtained with and without charcoal. What is important to notice is that both pass through the origin and the adsorption curve is, in addition, reversible. Apparently Rowe\* did not test the reversibility of his curves. In the author's view some such test of the reliability of the results is essential before they can be accepted and formulæ applied. The results obtained in the preliminary work where less care was taken in using the gauge, in purifying the nitrogen, and where the charcoal was not evacuated between each two points

\* Phil. Mag. i. p. 109 (1926).

on the curve, were not reproducible nor was any curve reversible, and, if the present results are taken as correct, large relative errors were committed. The acceptance or rejection of a particular formula on such results would have been quite unwarranted.

It will be seen that the nitrogen adsorption curve shows the quantity of nitrogen adsorbed to be a linear function of the pressure, i. e.  $q = Kp$ . These results show  $K$  to have the value 0.023 when  $q$  is in  $\frac{\text{mgrs.}}{\text{gram}}$  and  $p$  in mm. of mercury.

This is in agreement with the results of Claude\*, who also found at  $-183^\circ \text{C}$ . a linear relation between quantity of nitrogen adsorbed and the pressure in the low pressure region. The Freundlich adsorption formula is  $q = Kp^{1/n}$ . If this formula applies to the present results, then  $n=1$  for nitrogen in this pressure region.

The results show that equilibrium is rapidly attained and is set up from either direction with completeness in a time not greater than that required for equalization of pressure throughout the apparatus employed. They show also, incidentally, that nitrogen is completely and readily recoverable from charcoal at ordinary temperatures by evacuation. For, if this were not so, point one, obtained on the nitrogen-free charcoal, would not lie on the same curve as the other points, nor would the curve be regular if a variable amount of nitrogen were left in the charcoal after evacuating for each new point.

#### SUMMARY.

1. The isotherm for nitrogen and charcoal at  $25^\circ \text{C}$ . has been determined between the pressure limits  $2 \times 10^{-4}$  and  $1.3 \times 10^{-2}$  mm. of Hg.
2. At this temperature and in this pressure region the quantity of nitrogen adsorbed is a linear function of the pressure.
3. The isotherm is reversible and equilibrium is rapidly attained.

The author wishes in conclusion to express his best thanks to Professor A. J. Alimand for helpful criticism throughout the work.

University of London,  
King's College,  
May 1926.

\* *Comptes Rendus*, clviii. p. 861 (1914).

CXV. *On Sir J. J. Thomson's Model of a Light-Quantum.*  
*By Prof. N. P. KASTERIN, Research Institute of the  
 1 Moscow University\*.*

IT is commonly accepted that the quantum theory is almost incompatible with Maxwell's equations ("Clerk Maxwell's Electromagnetic Theory," by H. A. Lorentz, the Rede Lecture, 1923, p. 34); however, Sir J. J. Thomson † constructed a most valuable model of a light-quantum which, as will be shown, is formally consistent with the system of Maxwell's equations.

By the way of examining the simplest case of a light-quantum, we shall explain the difference of the Faraday-Maxwell-J. J. Thomson's electrodynamics from the usual Maxwell-Hertz-Lorentz's interpretation of an electromagnetic field, the form of the differential equations for the free æther being the same in both theories.

The light-quantum in the model of Sir J. J. Thomson consists in a ring-shaped Faraday tube moving with the speed of light at right angles to its own plane. The ring is preceded and followed by ordinary waves of feeble intensity; their wave-length is equal to the circumference of the ring. The energy contained in such a ring will be of the form  $\hbar\nu$  (Planck's law) if we admit, with Sir J. J. Thomson, that the cross-section of the tube is proportional to the square of the radius of the ring.

These two fundamental laws, as will be shown, are formally in accordance with the system of Maxwell's equations under the condition that we accept Sir J. J. Thomson's interpretation of an electromagnetic field.

Let  $\mathbf{E}_a$  (fig. 1) be a closed ring-shaped Faraday tube referred to fixed axes. Let us suppose that at  $t=0$  the plane of the ring coincides with the plane ZOY, and that  $\mathbf{u}_z$  is the velocity of the ring. The Maxwell's equations for the free æther are of the form

$$\operatorname{div} \mathbf{E} = 0, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

$$\operatorname{curl} \mathbf{M} = \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t}, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (2)$$

$$\operatorname{div} \mathbf{M} = 0, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

$$\operatorname{curl} \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{M}}{\partial t}, \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (4)$$

\* Communicated by the Author.

† "A Suggestion as to the Structure of Light," Phil. Mag. [6] xlviii. p. 737 (1924); "The Structure of Light," Phil. Mag. I. p. 1182 (1925).

where  $c$  is the velocity of light,  $\mathbf{E}$  the electric and  $\mathbf{M}$  the magnetic intensity. In the case of stationary motion the operation  $\frac{1}{c} \frac{\partial}{\partial t}$  will be replaced by  $-\beta_x \frac{\partial}{\partial x}$  if  $\beta_x = \frac{u_x}{c}$ , and the equations (2) and (4) will be transformed into

$$\operatorname{curl} \bar{\mathbf{M}} = 0 \quad \dots \dots \dots \quad (2')$$

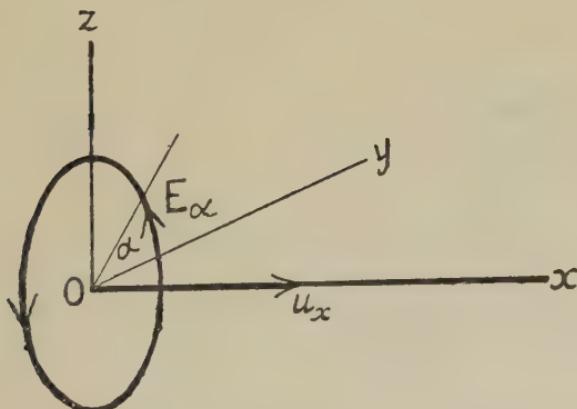
$$\text{and} \quad \operatorname{curl} \bar{\mathbf{E}} = 0, \quad \dots \dots \dots \quad (4')$$

where  $\bar{\mathbf{M}}$  has for components

$$\mathbf{M}_x, \mathbf{M}_y + \beta_x \mathbf{E}_z, \mathbf{M}_z - \beta_x \mathbf{E}_y$$

$$\text{and} \quad \bar{\mathbf{E}} \dots \dots \mathbf{E}_x, \mathbf{E}_y - \beta_x \mathbf{M}_z, \mathbf{E}_z + \beta_x \mathbf{M}_y.$$

Fig. 1.



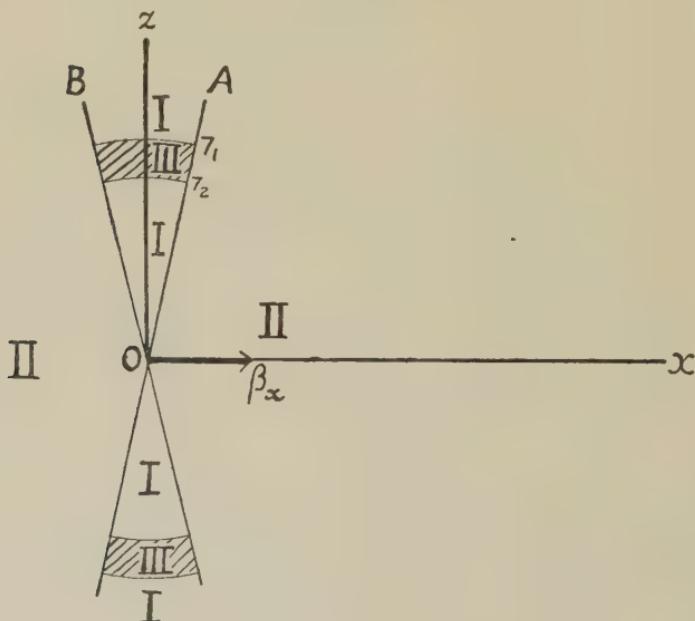
The simplest solutions of the equations (2') and (4') are the following:  $\bar{\mathbf{M}}=0$  and  $\bar{\mathbf{E}}=0$  for the whole space. Now  $\bar{\mathbf{M}}=0$  gives  $\mathbf{M}_x=0$ ,  $\mathbf{M}_y=-\beta_x \mathbf{E}_z$ , and  $\mathbf{M}_z=\beta_x \mathbf{E}_y$ . Since  $\bar{\mathbf{E}}=0$ , we have  $\mathbf{E}_x=0$ ,  $\mathbf{E}_y(1-\beta_x^2)=0$ , and  $\mathbf{E}_z(1-\beta_x^2)=0$ . These equations can be satisfied by two different suppositions:

$$\mathbf{E}_x=0, \mathbf{E}_y=0, \mathbf{E}_z=0; \text{ or } \mathbf{E}_x=0, \mathbf{E}_y \neq 0, \mathbf{E}_z \neq 0, 1-\beta_x^2=0.$$

Let us divide the whole space round the point O into three parts:—Part I, annular space between two cones (fig. 2), obtained by rotation of OA and OB round the  $x$ -axis, having a common vertex at O, the angle AOB being infinitesimal. Part II, the inside of the above-mentioned cones. Part III is taken out of I by the spheres of  $r_1$  and  $r_2$ , with the centre

at O. For parts I and II we take the first solution of the equations (2') and (4'), i.e.  $\mathbf{E}_x=0$ ,  $\mathbf{E}_y=0$ ,  $\mathbf{E}_z=0$ ; hence  $\mathbf{M}_x=0$ ,  $\mathbf{M}_y=0$ ,  $\mathbf{M}_z=0$ . For the region III we take the second solution:  $\mathbf{E}_x=0$ ,  $\mathbf{E}_y=-\mathbf{E}_a \sin \alpha$ ,  $\mathbf{E}_z=\mathbf{E}_a \cos \alpha$ ,  $\mathbf{E}_a \neq 0$ ,  $\beta_x=+1$ ; hence  $\mathbf{M}_x=0$ ,  $\mathbf{M}_y=-\mathbf{E}_a \cos \alpha$ ,  $\mathbf{M}_z=-\mathbf{E}_a \sin \alpha$ . Thus we obtain an electric field *only* in the region III. This field is moving with the velocity of light (first law of the light-quantum theory). If we transform the equation  $\operatorname{div} \mathbf{E}=0$ , using polar coordinates  $r$ ,  $\phi$ ,  $\alpha$ , we obtain  $\frac{\partial \mathbf{E}_a}{\partial \alpha}=0$ . Thus  $\mathbf{E}_a$  is a function of  $r$  only; the cross-section of the Faraday tube is constant.

Fig. 2.



The equation  $\operatorname{div} \mathbf{M}=0$ , which is also to be solved for the region III, after transformation takes the form

$$\frac{\partial}{\partial r}(r^2 \mathbf{M}_r)=0 \quad \dots \quad \dots \quad \dots \quad \dots \quad (5)$$

or

$$\frac{\partial}{\partial r}(r^2 \mathbf{E}_a)=0. \quad \dots \quad \dots \quad \dots \quad \dots \quad (5')$$

Here, namely in this equation (5), lies the divergence between the Maxwell-Hertz-Lorentz electrodynamics and the theory of Faraday-Maxwell-J. J. Thomson. From the standpoint of the first theory the equation (5) is valid in the whole space occupied by the free æther, and consequently will be valid in regions I and III and at their boundaries. So that if we admit  $\mathbf{E}_\alpha = 0$  and  $\mathbf{M}_r = 0$  for the region I, the

constant in the solution  $\mathbf{E}_\alpha = \frac{\text{const.}}{r^2}$  of the equation (5') for

the region III must also vanish. So, according to the first theory, there can be no electromagnetic field in the region III, since there is no field in the regions I and II. We cannot admit the existence of a field in the region I, as

it must have the form  $\mathbf{E}_\alpha = \frac{\text{const.}}{r^2}$ , which gives for the point O,  $\mathbf{E}_\alpha = \infty$ .

From the point of view of Sir J. J. Thomson's theory the structure of the field is *discontinuous*. The field consists in a system of Faraday tubes moving relatively to one another; the intensity of the magnetic field is determined by the intensity of the electric field and by the normal velocity  $\beta_n$  of the tube, from the equation  $\mathbf{M} = \beta_n \mathbf{E}$ . It follows (1) that the equation (2') is satisfied identically; (2) that the intensity  $\mathbf{M}$  has a definite value different from zero only where the Faraday tubes are in motion. The equation (3),  $\text{div } \mathbf{M} = 0$ , exists only where the Faraday tubes are in motion; in the rest of the free æther  $\mathbf{M}$  does not exist. If we admit the theory of J. J. Thomson, the equation  $\text{div } \mathbf{M} = 0$  must be satisfied in our case *only* in the region III up to its boundaries of II. At the boundary I-III we may have a discontinuity of  $\mathbf{M}_r$ , and consequently of  $\mathbf{E}_\alpha$ . Hence for the region III we may satisfy (5') by the supposition  $\mathbf{E}_\alpha r^2 = \text{finite constant}$ .

Calculating the energy of the ring, we obtain

$$\frac{1}{8\pi} (\mathbf{E}^2 + \mathbf{M}^2) \times \text{volume of the ring} = 2 \cdot \frac{1}{2}\epsilon \cdot \mathbf{E}_\alpha \cdot 2\pi r = \frac{2\pi^2\epsilon^2}{c\phi_0} \cdot \nu,$$

where  $\epsilon$  is the charge of the electron,  $\frac{\nu}{c} = \frac{1}{2\pi r}$ , and  $\epsilon/2\phi_0$

the constant of integration. Thus we obtain the second law of the light-quantum theory (Law of Planck).

From the preceding considerations we may conclude that the Maxwell's equations actually lead to the solution given by Sir J. J. Thomson.

It seems to me also that the difference between the

Maxwell-Hertz-Lorentz electromagnetic theory and the theory of Faraday-Maxwell-J. J. Thomson might be *analytically* formulated as follows :—(1) For the free æther the differential equations are the same in both theories, being the Maxwell's system :

$$\text{div } \mathbf{E} = 0, \quad \dots \dots \dots \quad (1)$$

$$\text{curl } \mathbf{M} = \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t}, \quad \dots \dots \dots \quad (2)$$

$$\text{div } \mathbf{M} = 0, \quad \dots \dots \dots \quad (3)$$

$$\text{and} \quad \text{curl } \mathbf{E} = \frac{1}{c} \frac{\partial \mathbf{M}}{\partial t}. \quad \dots \dots \dots \quad (4)$$

(2) The first theory postulated that all these equations are valid in the *whole* space filled by the free æther ; in the second theory the equation (3) occurs *only* where we have a moving electric field. Formulating this difference *geometrically*, we may say that the electric lines of force in the free æther are everywhere continuous, while the magnetic may be *discontinuous* : they must end on the boundaries dividing the moving Faraday tubes from those at rest. This circumstance gives the possibility of introducing *discontinuities* in electromagnetic field, and enormously increases the variability of the special instances, which satisfy the Maxwell systems of equations. The Maxwell equations, as it has been shown above, admit such forms of electromagnetic fields as have the same properties as the light-quanta.

It seems to me that this interpretation enables us to construct, on the basis of Maxwell's equations, investigating them for the case  $\beta_n^2 = 1$ , a *rational* quantum theory.

Research Institute of the  
1 Moscow University,  
1 April, 1926.

*CXVI. The Resistance of High-Frequency Circuits.* By  
R. R. RAMSEY, Ph.D., Professor of Physics, Indiana  
University\*.

THE resistance of a high-frequency circuit is apparently easy to determine. However, the separation of the resistance of the coil from that of the condenser is a difficult matter.

It has been customary to consider the resistance of the condenser small enough to be neglected, so that the entire resistance of the circuit is ascribed to the coil.

The first attempt to measure the resistance of a condenser at high frequency was made a little more than a year ago by Weyl and Harris (Institute of Radio Engineers, Proc. vol. xiii. p. 109, Feb., 1925). In this work the resistance of a rectangular coil approximately eighteen feet by twenty-five feet was calculated, assuming the resistance of the rectangle at the given frequency to be the same as the high frequency resistance of a straight wire of the same diameter, whose length was the same as the perimeter of the coil. The resistance obtained in this manner varied with the capacity of the condenser from one ohm at .0005 microfarad to about twenty ohms at .00005 microfarad.

Callis (Phil. Mag. vol. i. p. 428, Feb. 1926) has made measurements in which he used coils made of No. 36 and No. 40 copper wire. The method used was to measure the resistance of a circuit with a coil and condenser at a given setting using the resistance variation method, then to measure the resistance of the circuit again after the first coil had been replaced by one made exactly like the first. Then the two were connected in series opposition and their position adjusted, so the combined inductance of the two was the same as the inductance of a single coil, and the combined resistance was measured again. From these results the resistance of the condenser could be eliminated and the resistance of the coils determined. Since the results gave the resistance of the coils to be the same as the D.C. resistance, it was assumed that the resistance of small wire wound in a coil was the same as the resistance of the wire when straight, which was very close to its D.C. resistance at a frequency of one million. From these same equations the resistance of the condenser was determined. It was found that the resistance of a

\* Communicated by the Author.

41 plate variable condenser of the "low loss" type varied from 1·5 ohms at ·001 microfarad capacity to 15 ohms at ·00001 microfarad.

Maibauser and Taylor (Phys. Rev. vol. xxvii. p. 251, 1926), in the abstract of a paper presented before the American Physical Society, state that they have found the resistance of a variable condenser to be so large that the usual assumption that the resistance of the condenser is small enough to be neglected was not justified. However, the abstract does not give the values found.

All these results are much larger than the usual assumption,—so much larger that they may be said to be revolutionary. These experimenters find that the resistance of a good variable condenser varies from near one ohm at full capacity to fifteen or more at small capacity. The resistance varies as the reciprocal of the capacity, and the resistance may be said to be proportional to the reciprocal of the capacity as a very close approximation to the law.

The writer has tried to devise some circuit so as to verify these results. He tried measuring condensers in series and in multiple but could not get a check on the results. If one stops to calculate the resistance of condensers in series or in multiple, assuming that the resistance is proportional to the reciprocal of the capacity, one will find that the resistance of two condensers is equal to the resistance of one condenser. Thus when one condenser was replaced by two in parallel or in series, it was found that the resistance of the two was the same as that of one condenser. If the resistance of a condenser is negligibly small or zero, this is true also.

In order to get a check it was necessary to resort to heat measurements. The condenser or coil was placed in one bulb of a differential air thermometer while a known D.C. resistance was placed in the second bulb. The thermometer was made of two pyrex glass beakers inverted and sealed to glass plates. Through each glass plate three holes were drilled. In two of these holes electrical connexions were sealed, and in the third a glass tube was sealed. By connecting the glass tubes to a U-tube which contained a small amount of water, the relative pressure of the air in the beakers could be determined. Two T-tubes were placed above the U-tube, one under each beaker. By opening these T-tubes the pressure of the air in the beaker could be made equal to the pressure of the atmosphere.

The beakers were sealed to the glass plates with beeswax. At times there was some difficulty in getting the connexion air-tight. This was tested by noting whether the pressure

would become equal after a run. If there was evidence that one of the beakers leaked the result was discarded.

The coil or condenser under investigation was placed in one of the beakers and electrical connexions were made with solder. In the second beaker a known D.C. resistance was placed and soldered to the electrical connexions. It was found that when a coil was under investigation the best D.C. resistance to use was a coil which was an exact duplicate of the first coil. When the resistance of a condenser was being measured a short piece of "cromel" resistance wire, 3·4 ohms, was connected to the terminals in the D.C. beaker.

When making a measurement the procedure was as follows:—The coil or condenser was placed in the beaker and connected in a high-frequency circuit which was inductively connected to an oscillating circuit driven by a five-watt tube. The high-frequency circuit was adjusted to the proper current value. The approximate value of the D.C. current was found and then the apparatus was left for some time to cool down to the temperature of the room, the two side T tubes being open. In an hour or more the run proper was made. The side T-tubes were closed and the high-frequency generator was started. The D.C. current was turned on and adjusted so as to keep the pressure equal, as indicated by the water in the U-tube. After some minutes when final equilibrium was obtained the two ammeters were read. The high-frequency ammeter was a Weston 1·5 ampere thermo-ammeter which was correct for D.C. current and guaranteed by the maker to be accurate for 1500 kilocycle current. For small values of radio-frequency current a General Radio 250 milliamperes hot wire milliammeter was used. To measure D.C. current a Weston ammeter was placed in the circuit.

When thermal equilibrium is obtained the heat produced in one beaker is equal to the heat produced in the second beaker, assuming the thermal constants of the two beakers to be the same. Then  $I^2R = i^2r$ , where I and R refer to the current and resistance in the high-frequency circuit and  $i$  and  $r$  refer to the current and resistance in the D.C. circuit. Then we have the resistance of the radio-frequency circuit  $R = (i^2r)/I^2$ . Any dielectric losses, eddy current losses, or resistance losses will appear as heat. R, the resistance of the circuit, is the series resistance in the circuit which will produce the same heat as all these effects.

The accuracy of heat measurements is not as great as the accuracy of ordinary resistance measurements, and the

accuracy of these measurements is not as great as might be desired, but they are sufficiently accurate to indicate the approximate values and to settle the point in question.

First, coils were measured, and it was found that the resistance of a coil is less than the resistance of the circuit obtained by the resistance variation method. This result indicates that the condenser must have a resistance which cannot be neglected. A condenser was then placed in the beaker and the resistance was found to be very small—about 0·1 ohm—the capacity of the condenser being .00008 microfarad. This indicates that the heat generated in the circuit is less than the total energy of the circuit.

Table I. gives the data taken using five different coils. A.C. resistance is the resistance of the coil measured by the resistance variation method, assuming the resistance of the condenser to be small. Resistance (Heat) is the resistance obtained by means of the calorimeter.

TABLE I.

*Resistance of Coils at 1000 kilocycles.*

Capacity of condenser in microfarads.	D.C. resistance.	A.C. resistance.	Resistance (Heat).	Inductance in microhenries.	Remarks.
Coils of No. 20 copper wire, 30 turns each.					
.00008	0·35	10·7	8·2	316	Two coils in series.
.00028	0·35	8·3	7·3	91	Two coils series opposition.
.00028	0·175	4·3	3·7	91	Single coil.
Coil of No. 30 copper wire, 20 turns.					
.00020	9·6	19·4	11·5	127	Single coil.
Coil of No. 40 copper wire, 14 turns.					
.00054	16·6	21·1	17·2	47	Single coil.
Coil of No. 40 copper wire, 30 turns.					
.00009	34·3	52·5	36·6	282	Single coil.

Each result given in the above table is the average of a number of separate determinations.

It will be noticed that in every case the resistance as measured by the heat method is less than that measured by the resistance-variation method. The high-frequency resistance of the coil was balanced against the D.C. resistance of a similar coil. As a check the connexions were interchanged so as to test the equality of the thermal constants of the two bulbs. It was found that within the accuracy of the method there was no difference. Instead of a duplicate coil in some cases, the coil was checked against a short piece of resistance wire. These results agreed with the results obtained by using duplicate coils. Since the results obtained by the two methods check, it shows that the resistance of the condenser as given in the following table can be relied upon, as it was necessary to use unsymmetrical circuits when measuring the resistance of the condenser. To make the two circuits and bulbs as symmetrical as possible, a dummy condenser was placed in the D.C. side with the resistance wire in order to make the thermal capacity of the contents of the two bulbs equal.

In Table II., given below, the average of a number of readings is given.

TABLE II.

*Resistance of a 11-Plate Condenser set at .00008 m.f.  
(about one-third maximum).*

	300 metres.	80 metres.	40 metres.	27 metres.
Highest .....	.15 ohm.			
Lowest .....	.05 "			
Mean .....	.098 ,	.06	.04	.06

The results for 80, 40 and 27 metres are too low, since the ammeter in all probability reads too high. In the work at 300 metres it was necessary to keep the current at or below .8 ampere, since the potential became so high that an arc started between the plates of the condenser when the current was .9 ampere.

After these results were taken the condenser was compared with three others made by different firms, and it was found that there was no appreciable difference between this condenser and the average condenser.

These results show that the resistance of a good radio condenser is not excessive and that the results of Weyl and Harris, and Callis are entirely too large. Their results must be explained in some other manner. The probable explanation is as follows:—The calorimeter method measures the energy that remains in the pyrex glass beaker. Any energy radiated through the glass will not cause heat. Therefore, there must be an appreciable amount of energy radiated from an ordinary circuit. In other words, there is a certain amount of resistance in the circuit which cannot be ascribed to either the condenser or to the coil.

Bloomington, Indiana, U.S.A.

April 6, 1926.

*CXVII. The Radioactivity of Potassium and its Geological Significance.* By ARTHUR HOLMES, D.Sc., A.R.C.S., F.G.S., University of Durham, and ROBERT W. LAWSON, D.Sc., F.Inst.P., University of Sheffield \*.

CONTENTS.

- I. The Problem of the Pre-Cambrian Granites.
- II. The Radioactive Constants of Rubidium and Potassium.
- III. The Emission of Energy by Rubidium and Potassium.
- IV. Possible Effects other than Thermal.
- V. The Average Thickness of the Continents.
- VI. The Nature of the Substratum.
- VII. Geological Time and Latent Heat.
- VIII. Conclusions.

*I. The Problem of the Pre-Cambrian Granites.*

IT is a well-known fact of geological history that the greatest and most widespread intrusions of granitic rocks were those which invaded the continental crust during the earlier Pre-Cambrian eras. According to Daly, more than nine-tenths of the world's granites are of Pre-Cambrian age †. In later ages the more voluminous intrusions of granite and granodiorite have been restricted to belts characterized by intense mountain-building movements, such, for example, as those known as the Caledonian, Hercynian, and Appalachian. The great Pre-Cambrian shields have not been visibly penetrated by granite on an

\* Communicated by the Authors.

† 'Igneous Rocks and their Origin,' p. 57 (1914).

important scale since the close of the Pre-Cambrian, except in the immediate neighbourhood of the bordering geo-synclines and mountain belts. Moreover, the earlier invasions were on a far greater scale than those that followed. The continents began as great granitic regions, and through them surged four or more successive waves of granitic magma at long intervals, gradually becoming less voluminous—or less penetrative—as time went on, until by the end of the Pre-Cambrian eras that particular manifestation of regional magmatic activity came to an end, so far as the levels of the crust which are accessible to observation are concerned.

It is easy at the present day to understand why there should be no evidence of the development of such magmas during the later geological periods, because the radioactivity of the rocks is insufficient to generate the necessary heat for the production, within the continents, of the enormous volumes of magma, which alone could ascend so high that denudation should afterwards be able to disclose the rocks consolidated from them. The condition for the occurrence of such phenomena would be a far greater continental thickness than we can justifiably assume. Incidentally, this consideration explains why, in the later periods, granitic magmas have been generated deep within the cores of mountain ranges, for such situations are precisely those in which, because of compression, the continental rocks have been locally thickened\*.

The problem thus arises as to how it was that such regional phenomena occurred, and occurred on a decreasing scale, during the Pre-Cambrian eras. Were the continents far thicker then than now, or was the radioactive generation of heat more potent to provide the necessary supplies? The first assumption would lead to the conception of highland continents which could never have come beneath the waves. Yet we know that the lands were then, as afterwards, subject to marine transgressions and recessions. The second assumption would lead to the conclusion that basaltic lavas should also have been more abundant than in more recent periods. Again we know that they were not, for the eruptions of plateau-basalts in North and South America, the Brito-Arctic region and the Deccan, which occurred between the beginning of the Jurassic and the middle of the Eocene, were on as vast a scale as anything of which we have evidence from the Pre-Cambrian.

\* A. Holmes, Geol. Mag. lxii. pp. 507 & 533-534 (1925).

The extra source of heat must therefore be looked for either in the former distribution of the radioactive elements, or in the presence in the granitic rocks of some radioactive element not specially characteristic of basaltic rocks. It was the latter consideration that led us to suspect potassium as a possible active thermal agent. The joint investigation, of which this paper is a record, was therefore undertaken. The surprising result has emerged that potassium, on account of its great abundance in the rocks, is an emitter of radio-thermal energy of the same order of importance as either uranium or thorium\*. Rubidium is clearly negligible from the geological standpoint on account of its extreme rarity, despite the fact that its total activity is greater than that of an equal amount of potassium.

It was thought possible that the radioactivity of potassium might have been greater in early geological time than it is now, and so have led to the extensive intrusions of granite that then took place. It is, however, not yet possible to draw any such conclusion from the available data, nor will it become possible, unless future investigations indicate that the activity is confined to a still undiscovered isotope, which has been appreciably wearing out during geological time. Unfortunately, the detection of an end-product (isotope of calcium) in old potassium minerals is not practicable, owing to the very slow rate of decay of potassium. Meanwhile, the problem of the Pre-Cambrian granites remains unsolved, though it is not improbable that the explanation lies in the formerly more uniform distribution of potassium through the depths of the continents. Later intrusions would inevitably tend to concentrate potassium, as well as uranium and thorium, towards the surface, and so to reduce the temperatures natural to the lower regions of the continents. Thus in the early ages the ascent of heat from the substratum beneath the continents would be more effective in promoting fusion than it is now.

## II. *The Radioactive Constants of Rubidium and Potassium.*

Of the alkali metals, only rubidium and potassium show a measurable radioactivity. Whereas potassium emits  $\beta$ -rays of greater penetrating power than rubidium, it is generally recognized that the total activity (ionization corresponding to complete absorption) of rubidium is greater than that of an equal amount of potassium, though the estimates of the total relative activities vary within wide limits (1·4/1—

\* A. Holmes & R. W. Lawson, 'Nature,' cxvii. p. 620 (1926).

Harkins and Guy, and 7/1—N. R. Campbell)\*. The considerations set forth in the preceding section were responsible for our undertaking an examination of the extent to which the elements rubidium and potassium have contributed towards the thermal history of the earth, and for this purpose it was necessary to ascertain the radioactive constants of these two elements as accurately as possible from the evidence hitherto accumulated.

In order to obtain the most reliable values of the radioactive constants for these two elements, we have carefully analysed the data available, with the results recorded below. We shall deal first with the velocity and energy of the  $\beta$ -rays emitted by the two substances, and then with their most probable half-value periods, before applying the results to the materials of the earth's crust.

The  $\beta$ -rays from rubidium are fairly homogeneous, and their mean velocity has been determined † by direct comparison of their deflexion in a magnetic field with that of the rays from RaE. In this way the velocity of the rays was found to be about  $0\cdot62 c$ . This result is supported by estimates based on measurements of the coefficient of absorption of the rubidium rays. Thus Hahn and Rothenbach ‡ found that the rays are slightly softer than the  $\beta$ -rays from radium, but distinctly harder than the  $\beta$ -rays from UX<sub>1</sub>, whence they estimated the velocity to be about  $0\cdot58$ – $0\cdot60 c$ . We obtain a result in substantial agreement with the above, if we apply Lenard's curves of absorption § of  $\beta$ -rays of different velocity to Hahn and Rothenbach's value ( $\mu=347 \text{ cm.}^{-1}$  aluminium) for the coefficient of absorption of the  $\beta$ -rays from rubidium. We shall therefore assume that the velocity of these rays is  $0\cdot60 c$ , or that the kinetic energy of a single  $\beta$ -ray is  $2\cdot04 \times 10^{-7}$  erg.

The  $\beta$ -rays from potassium do not appear to be quite so homogeneous as those from rubidium, the coefficient of absorption varying for different observers from about  $16 \text{ cm.}^{-1}$  to  $50 \text{ cm.}^{-1}$  aluminium ||. Since, however, the rays are on an average only slightly less penetrating than those from

\* N. R. Campbell, Proc. Cambr. Phil. Soc. xv. p. 11 (1909). E. Henriot, *C. R.* cxlviii. p. 910 (1909). W. D. Harkins & W. G. Guy, Proc. Nat. Acad. Sc. xi. p. 628 (1925). Full references to the earlier literature are given in the standard works of Rutherford, and of Meyer and Schweidler.

† K. Bergwitz, *Phys. Zeit.* xiv. p. 655 (1913).

‡ O. Hahn & M. Rothenbach, *Phys. Zeit.* xx. p. 194 (1919).

§ 'The Structure of the Atom,' Andrade, Appendix I. p. 296 (G. Bell, 1923).

|| Campbell, etc., *l. c.*

$\text{UX}_2$  ( $\mu = 14.4 \text{ cm.}^{-1}$  aluminium,  $v = \text{ca. } 0.92 c$ ), Hahn (*l. c.*) concludes that the average velocity of the  $\beta$ -rays from potassium cannot differ much from  $0.90 c$ . If we assume  $\mu$  to be about  $20 \text{ cm.}^{-1}$  aluminium, Lenard's curves indicate that the velocity will be about  $0.85 c$ , and this value probably makes sufficient allowance for the heterogeneous nature of the rays. The corresponding kinetic energy of a  $\beta$ -ray from potassium is, then,  $7.30 \times 10^{-7} \text{ erg}$ .

We next require the half-value periods (or disintegration constants) of rubidium and potassium. In the case of rubidium, Hahn and Rothenbach (*l. c.*) have compared the activity of the  $\beta$ -rays emitted by 1 gm. of the element with that of the  $\beta$ -rays from the amount of  $\text{UX}_1$  in equilibrium with 1 gm. of uranium. Since these two types of ray are of the same order of hardness, it follows that the ratio of the half-periods of rubidium and uranium will be inversely as their activities (viz. 1/15), so that the resulting half-value period of rubidium is  $7 \times 10^{10} \text{ years}$ . Strictly speaking, we must take account of the different values of  $k$  (no. of ions per cm.) for the rays from the two substances, and of the fact that the Loschmidt number (per gm.) is not the same for the two elements. We find the corrected value of  $T_{\text{Rb}}$  to be  $1.4 \times 10^{11} \text{ years}$ .

By using an extremely delicate apparatus, Hoffmann \* has compared the activities of rubidium and potassium with that of uranium, and he concludes that his measurements confirm the value of the half-period for rubidium given by Hahn and Rothenbach, though his results point to a slightly smaller value for  $T_{\text{Rb}}$ . From the point of view of the half-value periods of potassium and rubidium, Hoffmann's measurements are probably the most valuable yet available, for they lend themselves to an approximately absolute interpretation when certain plausible assumptions are made, though he does not appear to have applied them in this way. He used two arrangements: (a) Method I, in which the active material was distributed on a concentric cylinder a few cms. away from his spherical ionization chamber; and (b) Method II, in which the active material was placed in the bounding surface of his ionization chamber; this latter method, however, was not applicable to uranium, owing to the disturbing action of the  $\alpha$ -rays. In both methods the apparatus was filled with  $\text{CO}_2$  at 1300 mm. pressure.

From known data on the absorption of  $\beta$ -rays in  $\text{CO}_2$ , and by assuming the constancy of  $\mu/\rho$  for the  $\beta$ -rays from

\* G. Hoffmann, *Phys. Zeit.* xxiv. p. 475 (1923); *Zeit. f. Phys.* xxv. p. 177 (1924).

a given substance, we have applied corrections to Hoffmann's results to take account of the absorption of the rays in his apparatus and in the active film. Moreover, since the ionization produced by a  $\beta$ -ray per cm. of its path (i. e.  $k$ ) is approximately known for rays of different velocity, we have been able to calculate that the half-period of rubidium is about 25 times that of uranium ( $4.4 \times 10^9$  years), i. e.  $T_{Rb} = 1.1 \times 10^{11}$  years, using the results of Method I. The corresponding calculation using the results of Method II gives  $T_{Rb} = \text{ca. } 8 \times 10^{10}$  years. There is thus satisfactory agreement between the different estimates of the half-value period of rubidium.

It appears, then, that the half-period of rubidium cannot be far removed from  $T_{Rb} = 10^{11}$  years ( $\lambda = 6.9 \times 10^{-12} \text{ years}^{-1}$ ), and we shall make use of these values in our subsequent considerations.

Unfortunately, the data for potassium are not known to the same degree of accuracy as those for rubidium, and further work is desirable with this element. It has already been mentioned that the estimates of the total activity (corresponding to complete absorption) of rubidium relative to that of an equal weight of potassium vary between 7 and 1.4. If we assume that the total ionization produced by a  $\beta$ -ray is proportional to its initial energy, and take account of the difference of the Loschmidt number (per gm.) for these two elements, the above estimates of the total relative activities indicate that the half-value period of potassium is respectively 50 or 11 times that of rubidium. Assuming  $T_{Rb} = 10^{11}$  years, the corresponding values for potassium are  $T_K = 5 \times 10^{12}$  and  $1.1 \times 10^{12}$  years respectively. In deciding between these extreme values of the half-period of potassium we can again appeal to Hoffmann's delicate measurements, by applying corrections to his results in the manner indicated above for rubidium. From the results of Method I we find that the half-period of potassium is about 14 times that of rubidium, or 22 times according to Method II. Hoffmann's measurements thus indicate that the half-value period of potassium is  $T_K = 1.4 \times 10^{12}$  years (Method I), or  $2.2 \times 10^{12}$  years (Method II), the former value being probably the more reliable.

We do not believe that the correct value of  $T_K$  exceeds about  $2 \times 10^{12}$  years, and consider that the evidence points to  $T_K = 1.5 \times 10^{12}$  years ( $\lambda = 4.6 \times 10^{-13} \text{ year}^{-1}$ ) as being the most representative value in the present state of our knowledge. We shall assume these values of  $T_K$  and  $\lambda$  in what follows. It should be mentioned that Hahn and

Rothenbach's estimate of the half-period of potassium, based on the relative activities of potassium and rubidium, is from 3 to 7 times that of rubidium, but that they only intended to indicate the general order of magnitude of the result.

In our previous considerations we have assumed that the whole of potassium is radioactive, whereas theoretical considerations render it probable that the activity will be a property of the isotope  $K_{41}$ , rather than of  $K_{39}$ . The decision of this point must await further experimental investigation. Should the radioactivity be due to  $K_{41}$ , our previous estimate of the disintegration constant would require to be increased 20 times, so that we should have  $T = 7.5 \times 10^{10}$  years. Early Archæan rocks (age of the order and greater than  $10^9$  years)\* would then have been heated by the contained potassium slightly more than at present, but as the increase is not more than one per cent., it can be neglected in geothermal problems. Should the activity be due to a hitherto undiscovered isotope, of atomic weight say 40, its increased effect in early geological time might demand consideration.

### *III. The Emission of Energy by Rubidium and Potassium.*

We are now in a position to calculate the annual heat production of 1 gram of potassium and rubidium respectively, from which, by making use of the content in average rock of these two elements, we are able to calculate the annual heat production due to potassium and rubidium in each gram of average rock, and similarly for any other kind of rock. The calculations are embodied in the accompanying Table, and for comparison, the annual heat production due to uranium and to thorium (plus disintegration products) per gram of rock are included. The values assumed for the annual heat developed from 1 gram of uranium ( $0.79$  cal. per annum =  $9.0 \times 10^{-5}$  cal./hour) and from 1 gram of thorium ( $0.23$  cal. per annum =  $2.6 \times 10^{-5}$  cal./hour) have been calculated on the basis of the most recent data, and are in good accord with the values as found experimentally.

It is clear from the Table that the geothermal effect of rubidium is negligible, and the same holds for sodium, which has been found to be practically inactive. On the other hand, the heat developed by the potassium in rocks is comparable with that developed by uranium and by thorium, and must have exerted an important, if not a controlling influence on the igneous history of the earth.

\* A. Holmes, Phil. Mag. (7) i. p. 1074 (1926).

Element ...	URANIUM.	THORIUM.	POTASSIUM.	RUBIDIUM.
Loschmidt Number, N, atoms per gram.	.....	.....	$15.5 \times 10^{21}$	$7.09 \times 10^{21}$
Half-value Period, T, in years.	.....	.....	$15 \times 10^{11}$	$1 \times 10^{11}$
Disintegration Con- stant, $\lambda$ , year $^{-1}$ .	.....	.....	$4.6 \times 10^{-13}$	$69 \times 10^{-13}$
Annual Number of Atoms disinte- grating per gram, $n = \lambda N$ .	.....	.....	$7.1 \times 10^9$	$49 \times 10^9$
Kinetic Energy, E, ergs per $\beta$ -ray.	.....	.....	$7.30 \times 10^{-7}$	$2.04 \times 10^{-7}$
Energy liberated per gram per year, $nE/(4.19 \times 10^7)$ cal.	$(7900 \times 10^{-4})$	$(2300 \times 10^{-4})$	$1.24 \times 10^{-4}$	$2.38 \times 10^{-4}$
Average Igneous Rock.	Contents in grams per gram of average igneous rock *. 6 $\times 10^{-6}$ 15 $\times 10^{-6}$ 26,000 $\times 10^{-6}$ m $\times 10^{-6}$			
Average Granite.	Heat generated in cals. per gram of average igneous rock per year. 4.74 $\times 10^{-6}$ 3.45 $\times 10^{-6}$ 3.92 $\times 10^{-6}$ 2.38m $\times 10^{-10}$			
Average Plateau-basalt.	Contents in gm. per gram of average granite *. 9 $\times 10^{-6}$ 20 $\times 10^{-6}$ 34,000 $\times 10^{-6}$ n.d.			
	Heat generated in cals. per gram of average granite per year. 7.1 $\times 10^{-6}$ 4.6 $\times 10^{-6}$ 4.2 $\times 10^{-6}$ n.d.			
	Contents in gm. per gram of average plateau-basalt *. 2.2 $\times 10^{-6}$ 5 $\times 10^{-6}$ 8000 $\times 10^{-6}$ n.d.			
	Heat generated in cals. per gm. of average plateau- basalt per year. 1.7 $\times 10^{-6}$ 1.2 $\times 10^{-6}$ 1.0 $\times 10^{-6}$ n.d.			

Total Heat in Calories per Year generated in :-

$$\text{Average Igneous Rock} = 11.4 \times 10^{-6} \text{ per gm.} = 31.4 \times 10^{-6} \text{ per c.c.}$$

(density = 2.75).

$$\text{Average Granite} = 15.9 \times 10^{-6} \text{ per gm.} = 42.2 \times 10^{-6} \text{ per c.c.}$$

(density = 2.65).

$$\text{Average Plateau-Basalt} = 3.9 \times 10^{-6} \text{ per gm.} = 11.7 \times 10^{-6} \text{ per c.c.}$$

(density = 3).  $= 13.3 \times 10^{-6}$  per c.c. of eclogite,  
density = 3.4.

\* For the data for radium and thorium, see J. Joly, Phil. Mag. (6) xlvi. p. 819 (1924); and for radium alone, A. Holmes, Geol. Mag. lxii. p. 509 (1925). The figures for potassium are based on thousands of analyses of rocks from all parts of the world.

#### IV. Possible Effects other than Thermal.

It is a well-known fact that the coloration of pleochroic haloes is produced by the action of the  $\alpha$ -particles emitted from the central radioactive inclusion, and Lord Rayleigh \* has brought forward strong evidence that the colour of zircons, which are always radioactive, is produced in the same way. Since  $\beta$ -rays and  $\gamma$ -rays also produce colorations in minerals when the radiation is of sufficient intensity, it has been suggested that the colour of many minerals may be due to this cause, particularly in view of the widespread occurrence and  $\beta$ -radioactivity of potassium. These latter colorations, however, would be expected to require much longer periods for their development than those due to the much more energetic  $\alpha$ -particles. It is, in fact, theoretically possible that the depth of coloration due to the potassium radiation found in a pure potassium mineral free from other colouring agents may serve to give a qualitative idea of the age of the formation in which the mineral occurs, for undoubtedly long periods will be necessary before any colour could appreciably develop from this cause. In practice such effects are likely to be always masked by the presence of other colouring agents.

The more important question arises, however: Is any appreciable fraction of the energy of the radioactive rays used up in producing these colorations? If so, the thermal effect in the mineral will be less than the effect as calculated from the energy of the rays. In a recent Presidential Address before the Geological Society, this question was raised by Dr. J. W. Evans, who stated: "It is certain, however, that the whole of this energy is *not* converted into heat; much of it must be employed in effecting physical, chemical, or atomic changes in the surrounding rock. The substance of the ionized pleochroic haloes in mica is hundreds of thousands of times greater than the radioactive material in the zircon round which they are formed, and they must represent a relatively enormous absorption of energy."

We think, with Lord Rayleigh †, that the evidence decides conclusively against Dr. Evans's view. In all determinations of the heat developed by radium and by it and its disintegration products, the substance has been enclosed in a glass tube of sufficient thickness to absorb

\* R. J. Strutt, Proc. Roy. Soc. (A), lxxxix, p. 405 (1914).

† Lord Rayleigh, 'The Observatory,' p. 57, Feb. 1926.

the  $\alpha$ -rays completely, as well as more than 30 per cent. of the  $\beta$ -rays, and it is well-known that the glass container rapidly becomes coloured by the action of the rays, just as in the case of minerals. We should therefore expect that, if Dr. Evans's view were correct, the heat development as determined experimentally would be distinctly less than the value calculated from a knowledge of the number and energy of the rays involved; but this is far from being the case. Thus for radium alone, *i.e.* without disintegration products, the calculated heat development per gram of the element is 25.47 cals. per hour, whereas the measured value (Hess) is 25.2 cals. per hour, and this experimental value probably requires to be raised by 0.2 or 0.3 cal. per hour owing to incomplete absorption of the  $\gamma$ -rays from radium in the apparatus used\*. Moreover, the total heat developed by 1 gram of radium together with its short-lived products was found by Rutherford and Robinson to be 135 cals./hour, and by St. Meyer and Hess to be 137 cals./hour, both results probably being somewhat low owing to insufficient allowance for the effect of the  $\gamma$ -rays. Using the latest data, we have calculated the total heat production of radium per gram, including the short-lived products, on the assumption that all the energy is converted into heat, and we obtain the value 137.7 cals./hour. It seems safe to conclude from these results that the energy of the radioactive rays expended in the manner suggested by Dr. Evans does not amount to one per cent. of the total energy, and is probably not more than about one-tenth of this value.

#### V. *The Average Thickness of the Continents.*

The geological consequences of the radioactivity of potassium are clearly of great importance, for the heat generated within the rocks is now found to be considerably greater than the amounts hitherto calculated from uranium and thorium alone.

A maximum estimate of the mean thickness of the average rocks (*sial*) of the continents can be arrived at by equating the amount of heat escaping at the surface with the heat generated within the *sial*. Geothermal gradients are very variable†, but a reasonable average,

\* R. W. Lawson, 'Nature,' cxvi. p. 897 (1925).

† See R. A. Daly, Amer. Jour. Sc. v. p. 349 (1923); and B. Gutenberg, *Der Aufbau der Erde*, p. 52 (1925), for recent discussions of the data.

sufficiently good for our present purpose, is 35° C. per kilometre. Taking the conductivity as 0·006 C.G.S., the heat lost per annum from a column of 1 sq. cm. cross section amounts to 63 calories, and evidently this could be entirely supplied by 15 km. of average granite (density 2·65), or by 20 km. of average continental rock (density 2·75). On the assumption made, the thickness of the continents should, then, be less than 20 km., for in addition to the heat generated within them, heat must also ascend from the hotter rocks beneath. On no reasonable assumptions whatever is it now possible to admit an average continental thickness of as much as 30 km., though more than 20 km. may still be possible if the radioactivity of the rocks rapidly decreases downwards. Like the gradients, the actual thickness must, of course, vary through a wide range, but the average is now definitely limited. Yet, until recently, 30 km. or thereabouts has been the estimate most favoured by seismologists.

In 1924, for example, an attempt was made by Gutenberg\* to determine the thickness from measurements of surface waves of known period that had traversed the continental crust. Taking :—

$T$  as the thickness of the surface layer ;

$c_2 = 3\cdot2$  km./sec. as the velocity of distortional waves in the surface layer ;

$c_2' = 4\cdot4$  km./sec. as the velocity of distortional waves in the substratum ; and

$c = 3\cdot8$  km./sec. as the velocity of the surface waves having a period of 30 secs. ;

he found  $T = 30$  km. A recomputation by Stoneley gave  $T = 31\cdot18$  km.

Stoneley †, however, drew attention to a serious flaw in the method. He pointed out that, owing to dispersion effects, it is not  $c$ , the wave velocity, that is given by the earthquake records, but  $C$ , the group velocity. Jeffreys then applied the necessary corrections, and worked out the group velocities for Love waves in a surface layer corresponding to that of the continental crust ‡. He adopted a density of 2·7, and took  $c_2 = 3\cdot1$  km./sec. For the underlying material the corresponding data used were—density = 3·4;  $c_2' = 4\cdot2$  km./sec. There is a period for

\* B. Gutenberg, *Phys. Zeit.* xxv. pp. 377–381 (1924).

† R. Stoneley, M. N. Roy. Astr. Soc., *Geophysical Suppl.*, vol. i. No. 6, p. 280 (Dec. 1925).

‡ H. Jeffreys, M. N. Roy. Astr. Soc., *Geophys. Suppl.*, vol. i. No. 6, p. 282 (Dec. 1925).

which the group velocity of surface waves is a minimum, the value of the latter being just under 3 km./sec. on the data adopted. The corresponding period is approximately 10 secs. These data give  $T=15\cdot2$  km. The adoption of any reasonable figure for the continental density, other than 2.7, which is itself reasonable, would have made no serious difference to the estimate of thickness finally reached.

Applying the same method to other results recorded by Gutenberg \*, one finds that for Eurasia  $T$  varies from 10 to 20 km.; and for America from 11 to 19 km. The thickness  $T=15$  km. is therefore a good average. For the sub-oceanic regions a light surface layer ranging from 4 to 8 km. in thickness is indicated. Thus, provided that the densities of 2.7 and 3.4 are justified, the average thickness of the *sial* of the oceanic regions should be about 6 km.

Seismic and thermal evidence have thus again come into close agreement, and for two independent reasons. The 30 km. continent on which Joly founded his theory of the surface history of the earth has become considerably thinner. This conclusion does not, however, invalidate the theory in any way. On the contrary, it relieves the theory of certain embarrassing consequences, and to that extent fortifies it. On the original view developed before the radioactivity of potassium was taken into account, and before the revision of the seismological estimates, cooling of the substratum by conduction through the continents was thought to be of little importance, as the basal temperature was naturally not far from the fusion point of the rocks. With a 15 km. continent, however, the natural temperature of the base is hundreds of degrees below any possible fusion point, and consequently cooling of the substratum through the continents becomes an important process.

## VI. *The Nature of the Substratum.*

If we accept an average thickness of 15 km. for the continental crust, and of 6 km. for the surface layer of the ocean floor, it is easy to show from the principle of isostasy that the substratum must everywhere have a density ranging from 3.4 to 3.5 or even a little more. This is not a consequence of the circumstance that Jeffreys adopted 3.4 for the substratum in his work on surface waves. It follows independently from the recognition of

\* B. Gutenberg, *Der Aufbau der Erde* (1925), Table 49.

the thermal effects due to potassium and the limit which is hereby set to the average continental thickness. Moreover, Jeffreys adopted that particular figure because the velocities of both longitudinal and distortional waves correspond, once they penetrate beyond the lighter crust, to those characteristic of silicate rocks with a density of 3·4 or more \*.

Were the substratum, as Joly and one of the present writers formerly assumed, to have a density of about 3, then continents only 15 km. thick would be submerged beneath an overflow from the oceans. A very much higher substratum density is necessary to give the requisite buoyancy to the continents. One may now picture the surface layer ranging from little or nothing over the sites of the greatest oceanic deeps, to possibly 6 km. thick over the average oceanic regions; rising to 15 km. over the average continental regions, and reaching as much as 30 or 40 km. in regions like the Thibet Plateau and the Himalayas. High-standing areas like the latter can only exist without fusion at the base on the condition that the radioactive content of the underlying column of rocks is unusually low.

The material of the substratum has long been thought by petrologists to be of basaltic composition †. Basaltic lavas have been extruded more often and more abundantly than any other type, and with a striking uniformity of chemical composition ‡. They have, moreover, as already stated, shown no sign of becoming less voluminous during geological time. The parent rocks from which they come must therefore occur in a layer which is very thick compared with the known igneous rocks of basaltic composition. Furthermore, this layer must extend to depths at which the temperature is high enough to permit fusion to occur.

Now there is only one known kind of rock which has the composition of basalt or gabbro and a density of 3·4 or 3·5, and that is eclogite §. Thus the assumptions that the substratum is eclogite, a high-pressure facies of basalt, satisfies the isostatic, seismic and petrological data. The only alternative assumption, that the material is peridotite,

\* L. H. Adams & E. D. Williamson, *Jour. Franklin Inst.* excv. p. 520 (1923).

† R. A. Daly, 'Igneous Rocks and their Origin,' p. 164 (1914).

‡ H. S. Washington, *Bull. Geol. Soc. Amer.*, vol. 33, p. 797 (1922).

§ L. L. Permor, *Rec. Geol. Surv. India*, vol. xliii. p. 41 (1913).

P. Eskola, *Norsk. Geol. Tidssk.* vol. vi. p. 182 (1920-22).

fails to satisfy the petrological data, for it would leave the basalts of the whole of geological time entirely unexplained. No doubt at a certain depth peridotite comes into place, but a thick eclogite layer must generally intervene between the peridotite of the greater depths and the granitic and related rocks of the surface layer \*.

### VII. *Geological Time and Latent Heat.*

According to the theory of basaltic cycles, originated by Joly, heat accumulates in the substratum below the level at which the temperature is that of fusion, and so, by supplying latent heat, leads to the production of magma. The latent heat of basaltic material of density 3 is about 270 calories per c.c., and the time taken to supply the whole of this by internal radioactive heating at the rate of  $11.7 \times 10^{-6}$  calorie per year would evidently be about 23 million years. Joly † has attempted to apply a simple calculation of this sort to the problem of geological time, and since he took into consideration only uranium and thorium he naturally arrived at a longer estimate of the time required to supply the latent heat. Unfortunately, the method seems unlikely ever to lead to acceptable results for two reasons. We have now to consider the latent heat not of basalt or gabbro, but of their high-pressure equivalent, eclogite; and not merely of eclogite as we occasionally encounter it near the earth's surface, but eclogite at a pressure of thousands of atmospheres. Moreover, it seems somewhat improbable that exactly all the eclogite of the zone of fusion should become liquid during a single cycle. When half the latent heat has been supplied, half of the material will have changed to the liquid state; and as the magma rises, as it must do, into the zone of cooling above, it may consolidate and die out long before the rest of the substratum has altogether fused.

The amount of magma produced depends not only on the supply of latent heat, but on the thickness of the zone through which it is being supplied, and also on the rate at which it rises, by a process of crystal stoping

\* Except possibly at certain times in the earth's history when the peridotite below may have fused and risen through the eclogite. Such a condition would be unstable, for later the eclogite would fuse and rise again above the peridotite. See A. Holmes, Geol. Mag., July, 1926, p. 326.

† J. Joly, 'The Surface History of the Earth,' pp. 90-92 and 153 (1925).

into the cooler regions above. Indeed, the magma rises because the crystal debris liberated from the roof by corrosion along the crystal boundaries falls to the bottom and so displaces the liquid upwards. The magma is therefore always underlain by solid material (unless, exceptionally, the peridotite of still greater depths also becomes fluid and engulfs that material), and consequently there is always being generated a certain supply of magma. It is the ascent and consolidation of the accumulated magma that gives rise to the periodicity; and each cycle consists of a period of magma accumulation and ascent, followed by a period of cooling and the consequent descent of the level beneath which magma can form.

The process may be capable of mathematical treatment in such a way as to give an expression for time in terms of other quantities, but the latter involve matters on which we have absolutely no data. The thickness of the eclogite zone, for example, is not likely to be revealed by seismic evidence, because the density is practically identical with that of peridotite, and no significant difference in elastic constants is to be anticipated. Thus, as already stated in a former publication\*, there are good reasons for considering "that far-reaching hypotheses of this kind should not be regarded as providing any sort of method for estimating geological time, but should themselves be tested, and modified where necessary, by reference to the ascertained data of geological time-measurements."

### VIII. Conclusions.

(a) The velocities of the  $\beta$ -rays emitted by rubidium and potassium are respectively  $0.60 c$  and  $0.85 c$ . The corresponding kinetic energies are respectively  $2.04 \times 10^{-7}$  and  $7.30 \times 10^{-7}$  erg.

(b) On available data, the most probable half-value period of rubidium is  $T_{Rb} = 10^{11}$  years, and of potassium  $T_K = 1.5 \times 10^{12}$  years. The disintegration constants are  $\lambda_{Rb} = 6.9 \times 10^{-12}$  year $^{-1}$  for rubidium, and  $\lambda_K = 4.6 \times 10^{-13}$  year $^{-1}$  for potassium.

(c) As an emitter of radio-thermal energy in rocks, potassium is, in the aggregate, of the same order of importance as uranium or thorium.

\* A. Holmes, Phil. Mag. (7) i. p. 1072 (1926).

(d) The radioactivity of rubidium has no geological significance, on account of the rarity of the element.

(e) There is no reason to suppose that as much as one per cent. of the energy of radioactive rays (from whatever source) can be expended in any other way than by conversion into heat.

(f) The continental crust must be less than 30 km., and probably does not exceed 20 km. in average thickness, a result that agrees with a recent estimate of 15 km. due to Jeffreys.

(g) The substratum beneath the continents and the surface layer of the ocean floor are shown to consist most probably of eclogite, a high-pressure facies of basaltic rock, having a density of 3·4 to 3·5.

(h) The time required for the accumulation of the latent heat of the material of the substratum may be about 23 million years, but this result is of theoretical interest only, and provides at present no basis for the erection of a geological time-scale.

June 21, 1926.

*Note added Nov. 1, 1926.*—Since this paper was written, further information has become available bearing on the thickness and structure of the continental masses. The following communications should therefore be referred to. They point to an average continental thickness ranging from 20 km. to 30 km., the lower estimate being preferable for thermal reasons; and to a downward distribution of rock-types tentatively interpreted by Jeffreys as granite-basaltic glass-dunite; and alternatively interpreted by one of us (A. H.) as granite-diorite-eclogite-dunite.

A. Holmes: "Contributions to the Theory of Magmatic Cycles." Geol. Mag., July 1926, p. 306.

L. H. Adams and R. E. Gibson: "The Compressibilities of Dunite and of Basalt Glass and their Bearing on the Composition of the Earth." Proc. Nat. Acad. Sci. xii. p. 275 (1926).

H. Jeffreys: "The Structure of the Continents." Nature, Sept. 25, 1926, p. 443.

A. Holmes: *Ibid.* Oct. 23, 1926, p. 586.

The Presidential Address by Dr. J. W. Evans, which was cited in Section IV., has now been published in the Q.J.G.S. lxxxii. p. 60 (1926).

CXVIII. *On the Stresses in a Spoked Wheel under Loads applied to the Rim.* By Professor A. J. SUTTON PIPPARD, M.B.E., D.Sc., and J. F. BAKER, B.A., University College, Cardiff\*.

ONE of the commonest units employed in engineering construction is the wheel, consisting of a rim connected to a central boss or hub by a number of evenly spaced arms or spokes. In general these spokes are rigidly attached both to the rim and to the hub. In consequence, the analysis of the stresses in such a wheel is a matter of considerable importance, and while solutions have been obtained for certain particular cases † of loading, it does not appear that the general problem has received the attention which its interest and importance merits.

In the present paper is given an analysis of the stresses in such a wheel when it is held rigidly at the hub and subjected to any system of loads applied to the rim. Since the effects produced by a number of loads can be found by superimposing those due to the loads considered separately, it is only necessary to analyse the case of a single load, and this in turn can be considered as two loads, one acting tangentially and the other acting radially. The problem is therefore reduced to the analysis of the stresses under a tangential and a radial load, and these cases are considered separately.

The results obtained appear somewhat complex: this, in view of the general nature of the problem, is unavoidable, but the actual computation in any particular case, although somewhat long, is not difficult. It is necessary, however, to work to a considerable degree of accuracy.

Figure 1 indicates the type of wheel considered.

Let  $N$  = number of arms evenly spaced.

$2\theta$  = angle between arms.

$R$  = radius of rim measured to the centroid of its section.

$R_0$  = radius of hub.

$I$  = moment of inertia of the cross-section of the rim about its axis of bending.

\* Communicated by the Authors.

† Cp. "Stresses in the rim and arms of a Flywheel rotating at constant speed," J. Longbottom : Trans. Inst. of Engineers and Shipbuilders of Scotland, lxii. (1919). "Stresses in a uniformly rotating Flywheel," A. J. S. Pippard : Inst. Mech. Engs., Jan. 1924. "Stresses in a Flywheel due to acceleration," A. J. S. Pippard : Inst. Mech. Engs., Jan. 1926.

$I_a$  = moment of inertia of cross-section of an arm about its axis of bending.

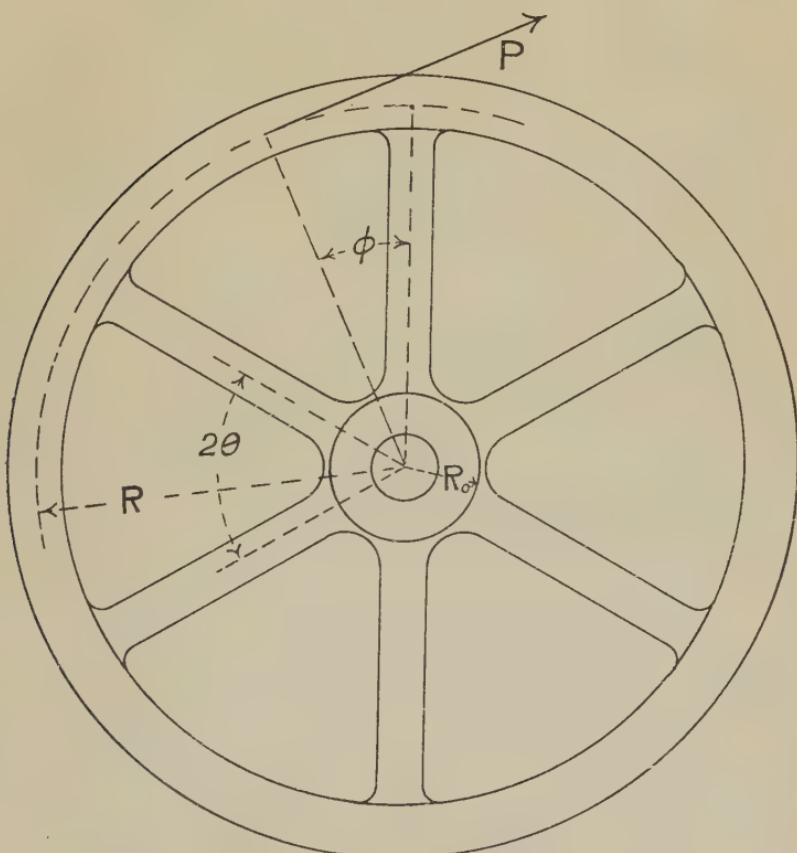
$a$  = area of cross-section of rim.

$a_0$  = area of cross-section of an arm.

$E$  = modulus of elasticity of material of rim and arm.

The method of solution adopted is to consider the wheel as a framework with a number of redundant reactions and to apply the Principle of Least Work to obtain the necessary equations.

Fig. 1.



The frame contains  $2N$  nodes, and so the number of bars required to make it just stiff is  $4N - 3$ . If the segments of the rim and the arms were pinned together and the arms pinned to the hub, the number of bars provided would be  $2N$ . Since the  $N$  nodes on the hub are fixed relatively to each other the hub itself is equivalent to  $(2N - 3)$  members and could be replaced by this number of bars

Hence the effective number of bars provided in the pinned framework is  $(4N - 3)$ , i.e. such a wheel would be just stiff. The continuity of the rim over the arms introduces one "redundancy" at each point, and since the arms are rigidly fixed to the rim and the hub, these attachments introduce two "redundancies" more for each arm. Hence the total number of "redundancies" in the frame is  $3N$ .

In fig. 2 let the reactions between the arms and the hub consist of

Forces  $H_1, H_2 \dots H_N$  tangential to the hub,

Forces  $T_1, T_2 \dots T_N$  acting along the arms,

Moments  $M_1, M_2 \dots M_N$ .

We shall treat  $H_1 \dots H_{N-1}, T_1 \dots T_{N-1}$ , and  $M_1 \dots M_{N-1}$  as "redundancies," giving  $3(N-1)$  of the total number present.  $H_N, T_N$ , and  $M_N$  are then determinate from the conditions of static equilibrium.

The remaining three "redundancies" are conveniently taken to be the resultant actions at a section of the rim just to the right of the Nth arm. These consist of a radial force  $V_0$ , a tangential force  $H_0$ , and a couple  $M_0$ .

There are then  $3(N+1)$  unknown forces and couples to be determined. Three of the essential equations are provided by a consideration of the static equilibrium of the wheel and the remaining  $3N$  by application of the Principle of Least Work as follows :—

Let  $U$  be the total strain energy of the wheel.

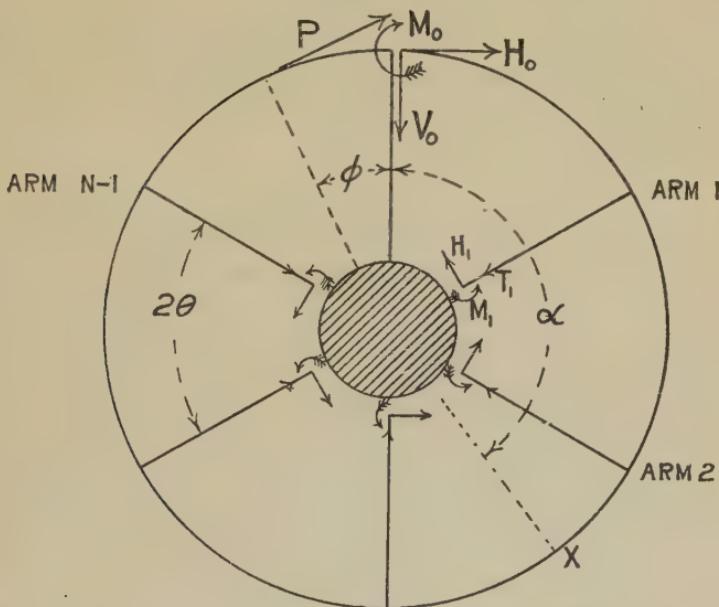
Then :

$$\left. \begin{array}{l} \frac{\partial U}{\partial H_0} = 0, \\ \frac{\partial U}{\partial V_0} = 0, \\ \frac{\partial U}{\partial M_0} = 0, \\ \frac{\partial U}{\partial H_1} = \frac{\partial U}{\partial H_2} = \dots \dots \dots \frac{\partial U}{\partial H_{N-1}} = 0, \\ \frac{\partial U}{\partial T_1} = \frac{\partial U}{\partial T_2} = \dots \dots \dots \frac{\partial U}{\partial T_{N-1}} = 0, \\ \frac{\partial U}{\partial M_1} = \frac{\partial U}{\partial M_2} = \dots \dots \dots \frac{\partial U}{\partial M_{N-1}} = 0. \end{array} \right\} \dots \dots (1)$$

*Case I.—Tangential load on rim.*

In fig. 2 let  $P$  be a tangential force acting on the rim between the  $(N-1)$ th and  $N$ th arms, and let its point of application be at an angular distance  $\phi$  from the  $N$ th arm.

Fig. 2.



Resolving forces perpendicular to, and along this arm and taking moments about the centre of the wheel, the conditions for static equilibrium are obtained as follows :—

$$(H_1 \cos 2\theta + H_2 \cos 4\theta \dots + H_N \cos 2N\theta) + (T_1 \sin 2\theta + T_2 \sin 4\theta \dots + T_{N-1} \sin 2(N-1)\theta) = P \cos \phi, \quad \dots \quad (2)$$

$$-(H_1 \sin 2\theta + H_2 \sin 4\theta \dots + H_{N-1} \sin 2(N-1)\theta) + (T_1 \cos 2\theta + T_2 \cos 4\theta \dots + T_N \cos 2N\theta) = P \sin \phi, \quad \dots \quad (3)$$

$$R_0(H_1 + H_2 \dots + H_N) + (M_1 + M_2 \dots + M_N) = PR. \quad \dots \quad (4)$$

Under the action of  $P$  the rim and arms of the wheel are subjected to bending, axial loads and shearing forces, all of which contribute to the strain energy. The effect of shearing force is, however, negligible compared with the others, and, following the usual custom, the strain energy due to bending and direct tension or compression will alone be considered.

The hub will be assumed to be rigid and will therefore contribute nothing to the strain energy. Also, in writing down the strain energy, the effect of the initial curvature of the rim will be neglected. The extra terms which would be involved would needlessly complicate the equations and their effect is entirely unimportant.

Let  $X$  be any point on the rim between the  $p$ th and  $(p+1)$ th arms, and let the angle between the radius to  $X$  and the  $N$ th arm be  $\alpha$ .

When  $\alpha < (2\pi - \phi)$  the compressive tangential force in the rim at  $X$  is

$$\begin{aligned} T_x = H_0 \cos \alpha + V_0 \sin \alpha \\ - \{H_1 \cos(\alpha - 2\theta) + H_2 \cos(\alpha - 4\theta) \dots H_p \cos(\alpha - 2p\theta)\} \\ + \{T_1 \sin(\alpha - 2\theta) + T_2 \sin(\alpha - 4\theta) \dots T_p \sin(\alpha - 2p\theta)\}. \end{aligned} \quad . . . \quad (5)$$

When  $\alpha > (2\pi - \phi)$  an extra term  $P \cos(\alpha + \phi)$  must be added.

When  $\alpha < (2\pi - \phi)$  the bending moment in the rim at  $X$  is

$$\begin{aligned} M_x = M_0 + H_0 R(1 - \cos \alpha) - V_0 R \sin \alpha \\ + R \{H_1 \cos(\alpha - 2\theta) + H_2 \cos(\alpha - 4\theta) \dots H_p \cos(\alpha - 2p\theta)\} \\ - R \{T_1 \sin(\alpha - 2\theta) + T_2 \sin(\alpha - 4\theta) \dots T_p \sin(\alpha - 2p\theta)\} \\ - R_0 \{H_1 + H_2 \dots H_p\} - \{M_1 + M_2 \dots M_p\}. \end{aligned} \quad . . . \quad (6)$$

When  $\alpha > (2\pi - \phi)$  an extra term  $PR(1 - \cos(\alpha + \phi))$  must be added.

Then the value of  $\frac{\partial U}{\partial M_0}$  for the segment of rim between  $\alpha = 2p\theta$  and  $\alpha = 2(p+1)\theta$  is

$$\frac{R}{EI} \int_{2p\theta}^{2(p+1)\theta} M_x \cdot \frac{\partial M_x}{\partial M_0} \cdot d\alpha,$$

and for the whole wheel, since the energy of the arms does not involve the terms  $M_0$ ,  $H_0$ , and  $V_0$ ,

$$\frac{\partial U}{\partial M_0} = \sum_{p=0}^{p=N-1} \frac{R}{EI} \int_{2p\theta}^{2(p+1)\theta} M_x \cdot \frac{\partial M_x}{\partial M_0} \cdot d\alpha = 0.$$

Similarly,

$$\frac{\partial U}{\partial H_0} = \sum_{p=0}^{p=N-1} \left[ \frac{R}{EI} \int_{2p\theta}^{2(p+1)\theta} M_x \cdot \frac{\partial M_x}{\partial H_0} \cdot d\alpha + \frac{R}{aE} \int_{2p\theta}^{2(p+1)\theta} T_x \cdot \frac{\partial T_x}{\partial H_0} \cdot d\alpha \right] = 0$$

and

$$\frac{\partial U}{\partial V_0} = \sum_{p=0}^{p=N-1} \left[ \frac{R}{EI} \int_{2p\theta}^{2(p+1)\theta} M_x \cdot \frac{\partial M_x}{\partial V_0} \cdot d\alpha + \frac{R}{aE} \int_{2p\theta}^{2(p+1)\theta} T_x \cdot \frac{\partial T_x}{\partial V_0} \cdot d\alpha \right] = 0$$

On integrating and summing these expressions after substituting the values of  $M_x$ ,  $T_x$ , etc., we obtain equations (7), (8), and (9).

In these equations we write

$$A = \frac{R^2}{EI},$$

$$B = \frac{1}{aE},$$

$$C = \frac{L^2}{EI_a},$$

$$D = \frac{1}{a_0 E},$$

$$L = (R - R_0).$$

$$\begin{aligned} & 2\pi(M_0 + RH_0) - R(T_1 + T_2 \dots T_N) \\ & + 2\theta\{R_0(H_1 + 2H_2 + 3H_3 \dots NH_N) + (M_1 + 2M_2 \dots NM_N)\} \\ & - PR(2\pi - \phi) = 0. \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (7) \end{aligned}$$

$$\begin{aligned} & (A + B) \left[ \pi RH_0 + \frac{R}{2} \{ H_1 \sin 2\theta + H_2 \sin 4\theta \dots H_{N-1} \sin 2(N-1)\theta \} \right. \\ & \quad \left. + R\theta \{ (H_1 \cos 2\theta + 2H_2 \cos 4\theta \dots NH_N) \right. \\ & \quad \left. + (T_1 \sin 2\theta + 2T_2 \sin 4\theta \dots (N-1)T_{N-1} \sin 2(N-1)\theta) \} \right. \\ & \quad \left. - \frac{PR}{2} \{ (2\pi - \phi) \cos \phi - \sin \phi \} \right] \end{aligned}$$

$$\begin{aligned} & - A \left[ \{ M_1 \sin 2\theta + M_2 \sin 4\theta \dots M_{N-1} \sin 2(N-1)\theta \} \right. \\ & \quad \left. + R_0 \{ H_1 \sin 2\theta + H_2 \sin 4\theta \dots H_{N-1} \sin 2(N-1)\theta \} \right. \\ & \quad \left. + PR \sin \phi \right] = 0. \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (8) \end{aligned}$$

$$\begin{aligned} & (A + B) \left[ \pi RV_0 + \frac{R}{2} \{ T_1 \sin 2\theta + T_2 \sin 4\theta \dots T_{N-1} \sin 2(N-1)\theta \} \right. \\ & \quad \left. + R\theta \{ H_1 \sin 2\theta + 2H_2 \sin 4\theta \dots (N-1)H_{N-1} \sin 2(N-1)\theta \} \right. \\ & \quad \left. - (T_1 \cos 2\theta + 2T_2 \cos 4\theta \dots NT_N) \} \right. \\ & \quad \left. + \frac{PR}{2} (2\pi - \phi) \sin \phi \right] \end{aligned}$$

$$\begin{aligned} & + A \left[ \{ M_1 \cos 2\theta + M_2 \cos 4\theta \dots M_N \} \right. \\ & \quad \left. + R_0 \{ H_1 \cos 2\theta + H_2 \cos 4\theta \dots H_N \} - PR \cos \phi \right] = 0. \quad (9) \end{aligned}$$

The three groups of equations obtained by differentiating the strain energy with respect to  $H_1 \dots H_{N-1}$ ,  $T_1 \dots T_{N-1}$ , and  $M_1 \dots M_{N-1}$  must now be considered. To form these equations we write down

$$\frac{\partial U}{\partial H_r} = 0, \quad \frac{\partial U}{\partial T_r} = 0, \quad \text{and} \quad \frac{\partial U}{\partial M_r} = 0,$$

and then by giving  $r$  all values from  $r=1$  to  $r=(N-1)$  inclusive all the required equations are obtained.

Since the bending and direct loads in the  $r$ th and  $N$ th arms are functions of  $M_r$ ,  $H_r$ , and  $T_r$  the strain energy of these arms will appear in the value of  $U$ .

Then

$$\begin{aligned} \frac{\partial U}{\partial M_r} = & \frac{1}{EI_a} \int_0^L \left( m_r \cdot \frac{\partial m_r}{\partial M_r} + m_n \cdot \frac{\partial m_n}{\partial M_r} \right) dx \\ & + \sum_p \frac{R}{EI} \int_{2p\theta}^{2(p+1)\theta} M_x \cdot \frac{\partial M_x}{\partial M_r} d\alpha, \end{aligned}$$

where  $m_r$  and  $m_n$  are the bending moments at any point in the  $r$ th and  $N$ th arms respectively, so that  $m_r = M_r - H_r x$ , where  $x$  is measured from the point where the arm joins the hub.

The second integral relates to the segment of the rim between the  $p$ th and  $(p+1)$ th arms, and after evaluation the terms composing it must be summed appropriately as follows :—

Terms in  $M_0$ ,  $H_0$ , and  $V_0$  from  $p=r$  to  $p=(N-1)$ .

Terms in  $M_q$ ,  $T_q$ , and  $H_q$  where  $q \leq r$  from  $p=r$  to  $p=(N-1)$   
and where  $q > r$  from  $p=q$  to  $p=(N-1)$ .

In a similar manner we may write

$$\begin{aligned} \frac{\partial U}{\partial H_r} = & \frac{1}{EI_a} \int_0^L \left( m_r \cdot \frac{\partial m_r}{\partial H_r} + m_n \cdot \frac{\partial m_n}{\partial H_r} \right) dx + \frac{1}{a_0 E} \int_0^L T_N \cdot \frac{\partial T_N}{\partial H_r} dx \\ & + \sum_p \left[ \frac{R}{EI} \int_{2p\theta}^{2(p+1)\theta} M_x \cdot \frac{\partial M_x}{\partial H_r} d\alpha + \frac{1}{aE} \int_{2p\theta}^{2(p+1)\theta} T_x \cdot \frac{\partial T_x}{\partial H_r} d\alpha \right] \end{aligned}$$

and

$$\begin{aligned} \frac{\partial U}{\partial T_r} = & \frac{1}{EI_a} \int_0^L \left( m_n \cdot \frac{\partial m_n}{\partial T_r} \right) dx + \frac{1}{a_0 E} \int_0^L \left( T_r + T_N \cdot \frac{\partial T_N}{\partial T_r} \right) dx \\ & + \sum_p \left[ \frac{R}{EI} \int_{2\theta}^{2(p+1)\theta} M_x \cdot \frac{\partial M_x}{\partial T_r} d\alpha + \frac{1}{aE} \int_{2\theta}^{2(p+1)\theta} T_x \cdot \frac{\partial T_x}{\partial T_r} d\alpha \right]. \end{aligned}$$

Upon substituting and integrating, and summing these

expressions the equations (10), (11), and (12) are obtained, where

$$\alpha_r = 2M_r - H_r L,$$

$$\alpha_n = 2M_N - H_N L,$$

$$\beta_r = 3M_r - 2H_r L,$$

$$\beta_n = 3M_N - 2H_N L, \text{ etc.}$$

$$\begin{aligned} A & \left[ 2(N-r)\theta M_0 + H_0 R \{ 2(N-r)\theta + \sin 2r\theta \} + V_0 R \{ 1 - \cos 2r\theta \}, \right. \\ & \quad \left. + R \sin 2r\theta \sum_{q=r}^{q=N} (H_q \cos 2q\theta + T_q \sin 2q\theta) \right. \\ & + R \cos 2r\theta \sum_{q=r}^{q=N} (T_q \cos 2q\theta - H_q \sin 2q\theta) - R \sum_{q=r}^{q=N} T_q \\ & \quad \left. + 2\theta \sum_{q=1}^{q=N-r} q(M_{r+q} + R_0 H_{r+q}) \right. \\ & \quad \left. - PR \{ \sin(2r\theta + \phi) + 2(N-r)\theta - \phi \} \right] + \frac{CR}{2L} (\alpha_n - \alpha_r) = 0. \end{aligned} \quad . . . \quad (10)$$

$$\begin{aligned} (A+B) & \left[ \frac{H_0 R}{2} \{ \sin 2r\theta + 2r\theta \cos 2r\theta \} + V_0 R (r\theta \sin 2r\theta) \right. \\ & \quad \left. - \frac{R}{2} \sum_{q=1}^{q=r-1} H_q \sin 2(r-q)\theta \right. \\ & \quad \left. + R\theta \sum_{q=1}^{q=r-1} (r-q) \{ T_q \sin 2(r-q)\theta - H_q \cos 2(r-q)\theta \} \right] \\ & + A \left[ -(M_0 + H_0 R) \sin 2r\theta + \sum_{q=1}^{q=r-1} (R_0 H_q + M_q (\sin 2(r-q)\theta)) \right. \\ & \quad \left. + \frac{C}{6} (\beta_n \cos 2r\theta - \beta_r) \right. \\ & \quad \left. - \frac{CR_0}{2L} (\alpha_r - \alpha_n \cos 2r\theta) + LD T_N \sin 2r\theta = 0. \right. \quad . . . \quad (11) \end{aligned}$$

$$\begin{aligned} (A+B) & \left[ H_0 R (r\theta \sin 2r\theta) + \frac{V_0 R}{2} \{ \sin 2r\theta - 2r\theta \cos 2r\theta \} \right. \\ & \quad \left. + \frac{R}{2} \sum_{q=1}^{q=r-1} T_q \sin 2(r-q)\theta \right. \\ & \quad \left. - R\theta \sum_{q=1}^{q=r-1} (r-q) \{ H_q \sin 2(r-q)\theta + T_q \cos 2(r-q)\theta \} \right] \\ & - A \left[ (M_0 + H_0 R) (1 - \cos 2r\theta) \right. \\ & \quad \left. - \sum_{q=1}^{q=r-1} (R_0 H_q + M_q) (1 - \cos 2(r-q)\theta) \right] + \frac{C}{6} (\beta_n \sin 2r\theta) \\ & + \frac{CR_0}{2L} \alpha_n \sin 2r\theta + LD(T_r - T_n \cos 2r\theta) = 0. \quad . . . \quad (12) \end{aligned}$$

The reduction of these equations to a useful form is a rather long process, but by operating with (10), (11), and (12) and the corresponding equations obtained when  $r$  is replaced by  $(r+1)$ , the results given in (13), (14), and (15) are obtained.

$$\alpha_{r+1} - \alpha_r$$

$$\begin{aligned}
 &= \frac{2AL}{CR} \left[ -2\theta(M_0 + H_0R) + H_0R\{\sin 2(r+1)\theta - \sin 2r\theta\} \right. \\
 &\quad \left. + V_0R\{\cos 2r\theta - \cos 2(r+1)\theta\} \right. \\
 &\quad \left. + 2\theta \sum_{q=1}^{q=r} (M_q + R_0H_q) + 2R\sin\theta \sum_{q=1}^{q=r} \{T_q \sin(2r-2q+1)\theta \right. \\
 &\quad \left. - H_q \cos(2r-2q+1)\theta\} \right]. 
 \end{aligned} \quad \dots \quad (13)$$

$$T_{r+1} - T_r \cos 2\theta$$

$$\begin{aligned}
 &= \frac{A+B}{2LD} \left[ H_0R\{\sin 2\theta \sin 2r\theta - 2\theta \sin 2(r+1)\theta\} \right. \\
 &\quad \left. + V_0R\{2\theta \cos 2(r+1)\theta - \sin 2\theta \cos 2r\theta\} \right. \\
 &\quad \left. + 2R\theta \sum_{q=1}^{q=r} \{H_q \sin 2(r-q+1)\theta + T_q \cos 2(r-q+1)\theta\} \right. \\
 &\quad \left. - R \sin 2\theta \sum_{q=1}^{q=r} \{T_q \cos 2(r-q)\theta + H_q \sin 2(r-q)\theta\} \right. \\
 &\quad \left. - \frac{R}{2} \{T_r \sin 2\theta + H_r \cos 2\theta\} \right] \\
 &\quad + \frac{A}{LD} \left[ (M_0 + H_0R) - \sum_{q=1}^{q=r} (M_q + R_0H_q) \right] (1 - \cos 2\theta) \\
 &\quad - \frac{C}{6LD} \beta_r \sin 2\theta - \frac{CR_0}{2L^2D} \cdot \alpha_r \sin 2\theta. \quad \dots \quad (14)
 \end{aligned}$$

$$\beta_{r+1} - \beta_r \cos 2\theta$$

$$\begin{aligned}
 &= \frac{3(A+B)}{C} \left[ H_0R\{\sin 2\theta \cos 2r\theta + 2\theta \cos 2(r+1)\theta\} \right. \\
 &\quad \left. + V_0R\{2\theta \sin 2(r+1)\theta + \sin 2\theta \sin 2r\theta\} \right. \\
 &\quad \left. + 2R\theta \sum_{q=1}^{q=r} \{T_q \sin 2(r-q+1)\theta - H_q \cos 2(r-q+1)\theta\} \right. \\
 &\quad \left. + R \sin 2\theta \sum_{q=1}^{q=r} \{T_q \sin 2(r-q)\theta - H_q \cos 2(r-q)\theta\} \right. \\
 &\quad \left. + \frac{R}{2} \{T_r \cos 2\theta - H_r \sin 2\theta\} \right] \\
 &\quad - \frac{6A}{C} \left[ (M_0 + H_0R) - \sum_{q=1}^{q=r} (M_q + R_0H_q) \right] \sin 2\theta \\
 &\quad + \frac{6LD}{C} T_r \sin 2\theta - \frac{3R_0}{L} (\alpha_{r+1} - \alpha_r \cos 2\theta) \quad \dots \quad (15)
 \end{aligned}$$

In order that the difference equations (13), (14), and (15) can be used it is necessary to determine values for  $\alpha_1$ ,  $\beta_1$ , and  $T_1$ . If, in equations (10), (11), and (12)  $r$  is put equal to unity, the resulting expressions can be reduced to simple forms by the use of equations (7), (8), and (9) and we obtain

$$\alpha_1 = \frac{2AL}{CR} [-2\theta(M_0 + H_0R) + H_0R \sin 2\theta + V_0R(1 - \cos 2\theta)] + \alpha_n. \quad (16)$$

$$\beta_1 = \frac{6(A+B)}{C} \left[ \frac{H_0R}{2} \sin 2\theta + H_0R\theta \cos 2\theta + V_0R\theta \sin 2\theta \right] - \frac{6A}{C} \sin 2\theta [M_0 + H_0R]$$

$$- \frac{3R_0}{L} (\alpha_1 - \alpha_n \cos 2\theta) + \beta_n \cos 2\theta + \frac{6LD}{C} (T_N \sin 2\theta). \quad (17)$$

$$T_1 = - \frac{A+B}{LD} \left[ H_0R\theta \sin 2\theta - V_0R\theta \cos 2\theta + \frac{V_0R}{2} \sin 2\theta \right] + \frac{A}{LD} (1 - \cos 2\theta) [M_0 + H_0R] - \frac{C}{6LD} \cdot \beta_n \sin 2\theta - \left( \frac{CR_0}{2L^2D} \cdot \sin 2\theta \right) \alpha_n + T_N \cos 2\theta. \quad (18)$$

These equations give  $\alpha_1$ ,  $\beta_1$ , and  $T_1$  in terms of the unknown quantities  $M_0$ ,  $H_0$ ,  $V_0$ ,  $\alpha_N$ ,  $\beta_N$ , and  $T_N$ , and having found them we have

$$H_1L = (3\alpha_1 - 2\beta_1) \quad \text{and} \quad M_1 = (2\alpha_1 - \beta_1).$$

Equations (13), (14), and (15) can now be used, since if we put  $r=1$  we obtain  $\alpha_2$ ,  $\beta_2$ , and  $T_2$  in terms of the same six quantities, and so  $H_2$  and  $M_2$ .

Successive substitution up to  $r=(N-2)$  enables all the quantities  $T_1, \dots, T_{N-1}$ ,  $H_1 \dots H_{N-1}$ , and  $M_1 \dots M_{N-1}$  to be found in terms of  $M_0$ ,  $\alpha_n$ , etc.

The static equations (2), (3), and (4) and the equations (7), (8), and (9) can now be used to furnish solutions for  $M_0$ ,  $H_0$ ,  $V_0$ ,  $T_N$ ,  $H_N$ , and  $M_N$ .

The equations so far obtained are perfectly general and may be used for the determination of the stress distribution in any wheel. The arithmetical work is rather long, but further simplification of the equations does not appear to be practicable and in any case does not lessen the labour of computation.

There are, however, two limiting cases which deserve attention, viz. the case of a rigid rim and the case of rigid arms.

*Wheel in which the rim is rigid.*

When the rim is rigid  $A=B=0$ , so that

$$\alpha_1 = \alpha_2 = \dots = \alpha_n.$$

And

$$\beta_1 = -\frac{3R_0}{L}(1-\cos 2\theta)\alpha_n + \beta_n \cos 2\theta + \frac{6LD}{C}T_N \sin 2\theta,$$

$$\beta_r = -\frac{3R_0}{L}(1-\cos 2r\theta)\alpha_n + \beta_n \cos 2r\theta + \frac{6LD}{C}T_N \sin 2r\theta.$$

While

$$T_1 = -\left(\frac{C}{6LD}\sin 2\theta\right)\beta_n - \left(\frac{CR_0}{2L^2D}\sin 2\theta\right)\alpha_n + T_N \cos 2\theta,$$

$$T_r = -\left(\frac{C}{6LD}\sin 2r\theta\right)\beta_n - \left(\frac{CR_0}{2L^2D}\sin 2r\theta\right)\alpha_n + T_N \cos 2r\theta.$$

Therefore

$$M_r = (2\alpha_r - \beta_r) = 2\alpha_n + \frac{3R_0}{L}(1-\cos 2r\theta)\alpha_n - \beta_n \cos 2r\theta - \frac{6LD}{C}T_N \sin 2r\theta$$

and

$$H_r = \frac{1}{L}\{3\alpha_r - 2\beta_r\} = \frac{1}{L}\left\{3\alpha_n + \frac{6R_0}{L}(1-\cos 2r\theta)\alpha_n - 2\beta_n \cos 2r\theta - \frac{12LD}{C}T_N \sin 2r\theta\right\}.$$

Using the static conditions in equations (2), (3), and (4) it is found that

$$H_N = P \cos \phi + \alpha_n \left\{ \frac{3}{L} + \frac{3R_0 N}{L^2} + \frac{CR_0 N}{4L^2 D} \right\} + \beta_n \left\{ \frac{N-2}{L} + \frac{CN}{12LD} \right\},$$

$$T_N = P \sin \phi - T_N \left\{ \frac{6DN}{C} + \frac{N-2}{2} \right\},$$

$$M_N = P(R - R_0 \cos \phi) - \alpha_n \left\{ \frac{R_0^2 N}{L^2} \left( 9 + \frac{C}{4D} \right) + \frac{6R_0 N}{L} + 2(N-1) \right\} - \beta_n \left\{ \frac{R_0 N}{L} \left( 1 + \frac{C}{12D} \right) + 1 \right\}.$$

And from these results

$$\alpha_n = \frac{PR}{2R_0N \left( 3 + \frac{3R_0}{L} + \frac{L}{R_0} \right)},$$

$$\beta_n = -\frac{3P}{N} \left[ \frac{L \cos \phi}{\left( 3 + \frac{C}{4D} \right)} + \frac{R}{2 \left( 3 + \frac{3R_0}{L} + \frac{L}{R_0} \right)} \right],$$

$$T_N = \frac{2P \sin \phi}{N \left( 1 + \frac{12D}{C} \right)}.$$

Now C is generally very large compared with D, so that we can put

$$\beta_n \doteq -\frac{3P}{N} \left[ \frac{L \cos \phi}{\frac{C}{4D}} + \frac{R}{2 \left( 3 + \frac{3R_0}{L} + \frac{L}{R_0} \right)} \right].$$

Then substituting for  $\alpha_n$ ,  $\beta_n$ , and  $T_N$ , we find that approximately

$$T_r = \frac{2P}{N} \{ \sin (2r\theta + \phi) \}.$$

This is a maximum when  $\sin (2r\theta + \phi)$  is a maximum, i.e. when  $(2r\theta + \phi) = \frac{\pi}{2}$  or  $\frac{3\pi}{2}$ .

Hence the maximum value of the tension in an arm occurs when  $\phi$  is such as to make the load act parallel to an arm, and the maximum value of T is then  $\frac{2P}{N}$ .

If the wheel has an even number of arms there will simultaneously occur an equal compression in the opposite arm to that carrying the maximum tension.

Again, it is found that

$$M_r = \frac{PR}{2N} \left[ \frac{\frac{2L}{R_0} + 3}{3 + \frac{3R_0}{L} + \frac{L}{R_0}} \right] + \frac{12PDL}{CN} [\cos (2r\theta + \phi)],$$

which is a maximum when  $\cos (2r\theta + \phi)$  is a maximum.

This occurs when  $\phi=0$  and  $r=N$ , i.e. when the load is applied at the end of one arm, and the value of M is then

$$M_{\max.} = \frac{PR}{2N} \left[ \frac{\frac{2L}{R_0} + 3}{\left( 3 + \frac{3R_0}{L} - \frac{L}{R_0} \right)} \right] + \frac{12PLD}{NC}.$$

Similarly,

$$H_r = \frac{3PR}{2NL} \left[ \frac{\frac{L}{R_0} + 2}{\left( 3 + \frac{3R_0}{L} + \frac{L}{R_0} \right)} \right] + \frac{24PD}{CN} \cos(2r\theta + \phi);$$

this is also a maximum when the load is applied to the end of one arm and

$$H_{\max.} = \frac{3PR}{2NL} \left[ \frac{\frac{L}{R_0} + 2}{\left( 3 + \frac{3R_0}{L} + \frac{L}{R_0} \right)} \right] + \frac{24PD}{CN}.$$

*Wheel in which the arms are rigid.*

When the arms are rigid and the rim is elastic any load  $P$  placed between the  $(N-1)$ th and  $N$ th arms will cause stresses only in these two arms.

Hence

$$T_1 = T_2 = \dots = T_{N-2} = 0,$$

$$M_1 = M_2 = \dots = M_{N-2} = 0,$$

$$H_1 = H_2 = \dots = H_{N-2} = 0.$$

The static equations (2), (3), and (4) then give

$$H_N = P \cos \phi - H_{N-1} \cos 2\theta + T_{N-1} \sin 2\theta,$$

$$T_N = P \sin \phi - T_{N-1} \cos 2\theta - H_{N-1} \sin 2\theta,$$

$$M_N = PR - M_{N-1} - R_0 \{ H_{N-1} (1 - \cos 2\theta) \\ + T_{N-1} \sin 2\theta + P \cos \phi \}.$$

Also, since  $M_0$ ,  $V_0$ , and  $H_0$  are all zero, we have, on substituting the values of  $H_N$ ,  $T_N$ , and  $M_N$  in (7), (8), and (9), the equations

$$H_{N-1} \left( \frac{R}{2} \sin 2\theta + R\theta \cos 2\theta - R_0 \sin 2\theta \right) - T_{N-1} (R\theta \sin 2\theta) \\ - M_{N-1} \sin 2\theta + \frac{PR}{2} (\sin \phi - \phi \cos \phi) = 0.$$

$$H_{N-1} \{ R_0 (1 - \cos 2\theta) - R\theta \sin 2\theta \} \\ + T_{N-1} \left\{ \frac{R}{2} \sin 2\theta - R\theta \cos 2\theta \right\} + M_{N-1} (1 - \cos 2\theta) \\ + \frac{PR}{2} \{ \phi \sin \phi - 2(1 - \cos \phi) \} = 0.$$

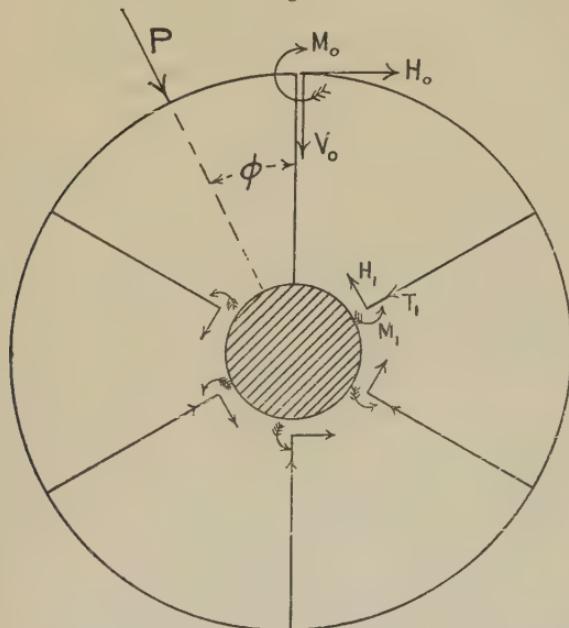
$$H_{N-1} \{ 2\theta R_0 - R \sin 2\theta \} + T_{N-1} \{ R (1 - \cos 2\theta) \} \\ + 2\theta M_{N-1} + PR (\sin \phi - \phi) = 0.$$

The general solution of these is rather long, but for any special case the coefficients of  $H_{N-1}$ ,  $T_{N-1}$ , and  $M_{N-1}$  are easily found and the particular solution readily obtained.  $H_N$ ,  $T_N$ , and  $M_N$  are then found from the static conditions.

*Case 2.—Radial load on rim.*

This case is shown in fig. 3 where a radial load  $P$  is applied between the  $(N-1)$ th and  $N$ th arms at a point defined by the angle  $\phi$  measured from the  $N$ th arm.

Fig. 3.



The conditions for static equilibrium of the wheel now become

$$(H_1 \cos 2\theta + H_2 \cos 4\theta \dots H_N) + (T_1 \sin 2\theta + T_2 \sin 4\theta \dots T_{N-1} \sin 2(N-1)\theta) = P \sin \phi \quad \dots \quad (19)$$

$$-(H_1 \sin 2\theta + H_2 \sin 4\theta \dots H_{N-1} \sin 2(N-1)\theta) + (T_1 \cos 2\theta + T_2 \cos 4\theta \dots T_N) = -P \cos \phi, \quad \dots \quad (20)$$

$$R_0(H_1 + H_2 \dots H_N) + (M_1 + M_2 \dots M_N) = 0. \quad \dots \quad (21)$$

The compressive tangential force in the rim, and the bending moment at a point  $\alpha$  from the  $N$ th arm when

$\alpha < (2\pi - \phi)$  will be the same as for Case I. and formulæ (5) and (6) are applicable.

When  $\alpha > (2\pi - \phi)$  the extra terms to be added to these equations are  $P \sin(\alpha + \phi)$  and  $-PR \sin(\alpha + \phi)$  respectively.

The equations derived from  $\frac{\partial U}{\partial M_0} = 0$ ,  $\frac{\partial U}{\partial H_0} = 0$ , and  $\frac{\partial U}{\partial V_0} = 0$  are, except for the terms involving  $P$ , of the same form as in the case of a tangential load and are given in (22), (23), and (24).

$$\begin{aligned} 2\pi(M_0 + RH_0) - R(T_1 + T_2 \dots T_N) \\ + 2\theta\{R_0(H_1 + 2H_2 + 3H_3 \dots NH_N) + (M_1 + 2M_2 \dots NM_N)\} \\ - PR = 0. \quad \dots \quad (22) \end{aligned}$$

$$\begin{aligned} (A + B) \left[ \pi RH_0 + \frac{R}{2} \{ H_1 \sin 2\theta \right. \\ \left. + H_2 \sin 4\theta \dots H_{N-1} \sin 2(N-1)\theta \} \right. \\ \left. + R\theta \{ (H_1 \cos 2\theta + 2H_2 \cos 4\theta \dots NH_N) \right. \\ \left. + (T_1 \sin 2\theta + 2T_2 \sin 4\theta \dots (N-1)T_{N-1} \sin 2(N-1)\theta) \} \right. \\ \left. - \frac{PR}{2} (2\pi - \phi) \sin \phi \right] \\ - A \left[ \{ M_1 \sin 2\theta + M_2 \sin 4\theta \dots M_{N-1} \sin 2(N-1)\theta \} \right. \\ \left. + R_0 \{ H_1 \sin 2\theta + H_2 \sin 4\theta \dots H_{N-1} \sin 2(N-1)\theta \} \right] = 0. \\ \quad \dots \quad (23) \end{aligned}$$

$$\begin{aligned} (A + B) \left[ \pi RV_0 + \frac{R}{2} \{ T_1 \sin 2\theta + T_2 \sin 4\theta \dots T_{N-1} \sin 2(N-1)\theta \} \right. \\ \left. + R\theta \{ (H_1 \sin 2\theta + 2H_2 \sin 4\theta \dots (N-1)H_{N-1} \sin 2(N-1)\theta) \right. \\ \left. - (T_1 \cos 2\theta + 2T_2 \cos 4\theta \dots NT_N) \} \right. \\ \left. + \frac{PR}{2} \{ \sin \phi + (2\pi - \phi) \cos \phi \} \right] \\ + A \left[ \{ M_1 \cos 2\theta + M_2 \cos 4\theta \dots M_N \} \right. \\ \left. + R_0 \{ H_1 \cos 2\theta + H_2 \cos 4\theta \dots H_N \} \right] = 0. \quad \dots \quad (24) \end{aligned}$$

The remainder of the work follows closely the treatment described in the first case and the results given in eqs. (13), (14), (15), (16), (17), and (18) can be used for the present type of loading.

Having found  $M_1$ ,  $H_1$ ,  $T_1$ , etc. the values must be substituted in equations (19), (20), and (21), and (22), (23), and (24) to solve for  $M_N$ ,  $H_N$ ,  $T_N$  and  $M_o$ ,  $H_o$ , and  $V_o$ .

The two special cases considered in the previous type of loading will now be examined.

### *Wheel in which the rim is rigid.*

The equations for  $M_r$ ,  $H_r$ , and  $T_r$  are as in the case of a tangential load, and from the equations of static equilibrium we find

$$H_N = P \sin \phi + \alpha_n \left\{ \frac{3}{L} + \frac{3R_0N}{L^2} + \frac{CR_0N}{4L^2D} \right\} + \beta_n \left\{ \frac{N-2}{L} + \frac{CN}{12LD} \right\},$$

$$T_N = -P \cos \phi - T_N \left\{ \frac{6DN}{C} + \frac{N-2}{2} \right\},$$

$$M_N = -PR_0 \sin \phi - \alpha_n \left\{ \frac{R_0^2N}{L^2} \left( 9 + \frac{C}{4D} \right) + \frac{6R_0N}{L} + 2(N-1) \right\},$$

$$- \beta_n \left\{ \frac{R_0N}{L} \left( 1 + \frac{C}{12D} \right) + 1 \right\}.$$

From these results

$$\alpha_n = 0,$$

$$\beta_n = -\frac{3P}{N} \left\{ \frac{L \sin \phi}{3 + \frac{C}{4D}} \right\},$$

$$T_N = -\frac{2P \cos \phi}{N \left( 1 + \frac{12D}{C} \right)}.$$

If  $\frac{C}{D}$  is very large it will be found that

$$H_{\max.} = \frac{24PD}{CN},$$

$$M_{\max.} = \frac{12PDL}{CN}.$$

These occur in the arm which is parallel to the load but are negligible since  $\frac{C}{D}$  is large.

The maximum value of  $T$  occurs when the load acts at the end of one arm and its value in that arm is  $-\frac{2P}{N}$ , i.e. it is compressive.

The value of  $T_r$  becomes

$$T_r = -\frac{2P}{N} (\cos 2r\theta + \phi),$$

giving the axial load in any arm.

*Wheel in which the arms are rigid.*

As in the first case,

$$T_1 = T_2 = \dots T_{N-2} = 0,$$

$$H_1 = H_2 = \dots H_{N-2} = 0,$$

$$M_1 = M_2 = \dots M_{N-2} = 0.$$

From the equations for static equilibrium we have

$$H_N = P \sin \phi - H_{N-1} \cos 2\theta + T_{N-1} \sin 2\theta,$$

$$T_N = -P \cos \phi - T_{N-1} \cos 2\theta - H_{N-1} \sin 2\theta,$$

$$M_N = -M_{N-1} - R_0 \{ H_{N-1} (1 - \cos 2\theta) + T_{N-1} \sin 2\theta + P \sin \phi \}.$$

And since  $M_0$ ,  $H_0$ , and  $V_0$  are all zero, we have from equations (22), (23), and (24) :

$$H_{N-1} \left( \frac{R}{2} \sin 2\theta + R\theta \cos 2\theta - R_0 \sin 2\theta \right)$$

$$-T_{N-1} (R\theta \sin 2\theta) - M_{N-1} \sin 2\theta - \frac{PR}{2} \phi \sin \phi = 0,$$

$$H_{N-1} \{ R_0 (1 - \cos 2\theta) - R\theta \sin 2\theta \}$$

$$+ T_{N-1} \left\{ \frac{R}{2} \sin 2\theta - R\theta \cos 2\theta \right\} + M_{N-1} (1 - \cos 2\theta)$$

$$- \frac{PR}{2} \{ \sin \phi + (4\pi - \phi) \cos \phi \} = 0,$$

$$H_{N-1} \{ 2\theta R_0 - R \sin 2\theta \} + T_{N-1} \{ R (1 - \cos 2\theta) \}$$

$$+ 2\theta M_{N-1} - PR \cos \phi = 0.$$

These, again, in any special case, can be readily solved, although the expressions for the general solution are somewhat cumbersome.

## Example of a wheel with two spokes.

As an example of the results obtained by the foregoing method of analysis a wheel with two spokes was investigated. The particulars assumed in making the calculations were as follows :

$$R_0 = 0.25 R,$$

$$\frac{A}{C} = 1,$$

$$\frac{C}{D} = 1080.$$

B was negligible compared with A.

These values give a rim of the same order of rigidity as the arms.

The load P was applied tangentially to the rim and the resultant actions were found for the two cases  $\phi=0$  and  $\phi=\pi$ .

By taking these two cases a check on the accuracy of the method was provided since the values of  $T_1$ ,  $M_1$ , and  $H_1$  in one case should become those of  $T_2$ ,  $M_2$ , and  $H_2$  in the other case, and *vice versa*.

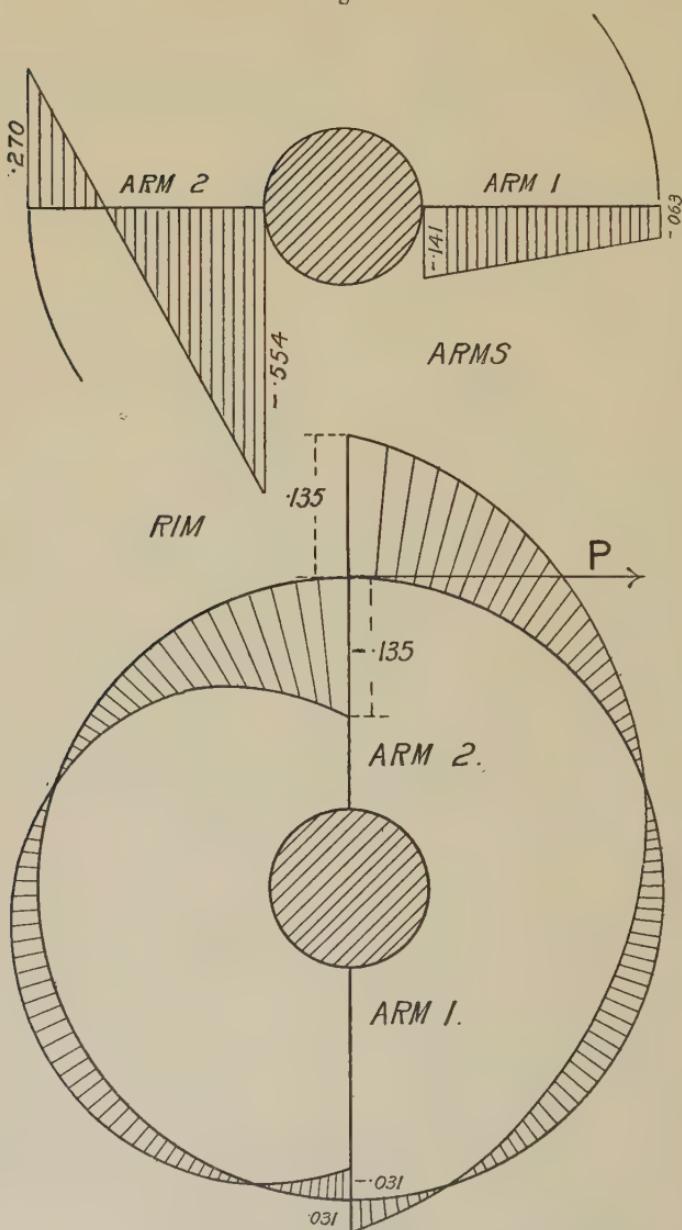
Further, the values of  $M_0$ ,  $H_0$ , and  $V_0$  for  $\phi=\pi$  can be deduced from the results of the analysis for  $\phi=0$  by calculating the actions in the rim just past the first arm.

The results are given in the following table :—

$\phi$ .	$\frac{M_0}{PR}$ .	$\frac{H_0}{P}$ .	$\frac{V_0}{P}$ .	$\frac{T_1}{P}$ .	$\frac{T_2}{P}$ .	$\frac{H_1}{P}$ .	$\frac{H_2}{P}$ .	$\frac{M_1}{PR}$ .	$\frac{M_2}{PR}$ .
0 .....	-·135	-·052	-·106	0	0	·104	1·104	·142	·554
$\pi$ .....	-·030	-·055	-·108	0	0	1·101	·101	·554	·141

The deduced values of  $M_0/PR$ ,  $H_0/P$ , and  $V_0/P$  are -·031, -·052, and -·106 respectively. Within the limits of accuracy adopted in calculation therefore the agreement of these and of the other quantities may be considered good.

Fig. 4.



*BENDING MOMENTS IN 2 ARMED WHEEL  
Ordinates give  $M/PR$*

The bending moment diagrams for the rim and arms have been plotted in fig. 4 for the case  $\phi=0$ .

CONCLUSION.

The analysis of the problem given in this paper has been kept in as general a form as possible so that a complete solution might be presented. This attempt at generality has made the results appear to be complex, and although the arithmetical work required in a particular case is straightforward in character it must be done with considerable accuracy since small differences of large numbers are involved.

From the standpoint of design it is generally sufficient to obtain results of an approximate nature, and it is hoped at a later date to develop the results of this analysis, by the introduction of simplifying assumptions, to a form which will make them more readily available for application to design.

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**CXIX. Critical Potentials and X-ray Term Values.** By  
ANN CATHERINE DAVIES, *D.Sc.*, and Prof. FRANK HORTON,  
*Sc.D., F.R.S.\**

THE critical potentials for the production of soft X-rays from solids have been investigated during the course of the last few years by several investigators†. The method employed in such investigations consists essentially in bombarding a solid target of the element under test by electrons from a hot filament, the energy of these electrons

\* Communicated by the Authors.

† O. W. Richardson and C. B. Bazzoni, *Phil. Mag.* xlii. p. 1015 (1921).  
O. W. Richardson and F. C. Chalklin, *Proc. Roy. Soc. A*, cx. p. 247 (1926).

E. H. Kurth, *Phys. Rev.* xviii. p. 461 (1921).

F. L. Mohler and P. D. Foote, *Sci. Papers, Bur. of Standards*, No. 425 (1922).

J. Holtsmark, *Phys. Zeit.* xxiii. p. 232 (1922), and *Phys. Zeit.* xxiv. p. 225 (1923).

J. C. McLennan and M. L. Clark, *Proc. Roy. Soc. A*, cii. p. 389 (1923).

U. Andrewes, A. C. Davies and F. Horton, *Phil. Mag.* xlvi. p. 721 (1923); *Proc. Roy. Soc. A*, cx. p. 64 (1926).

C. B. Bazzoni and C. T. Chu, *Journal Franklin Institute*, 197. p. 183 (1924).

C. T. Chu, *Journal Franklin Institute*, 200. p. 615 (1925).

G. K. Rollefson, *Phys. Rev.* xxiii. p. 35 (1924), & xxv. p. 740 (1925).

J. C. Boyce, *Phys. Rev.* xxiii. p. 575 (1924).

M. Levi, *Trans. R. S. Canada*, xviii. p. 159 (1924).

C. H. Thomas, *Phys. Rev.* xxv. p. 322 (1925), & xxvi. p. 739 (1925).

being varied by varying the voltage used to accelerate them. The radiation emitted as the result of the bombardment is measured by its photoelectric action on a suitably placed electrode, and the ratio of the photoelectric current per unit bombarding current for any target is plotted against the voltage corresponding to the energy of the electrons bombarding the target, obtained by adding a correction for various factors to the value of the applied accelerating potential difference. The voltages at which discontinuities in the resulting curves occur are taken as critical points indicating stages in the excitation of the targets, and therefore as being related to the different "shells" of electrons in the atoms of the targets, and to their X-ray levels.

The outstanding feature of the curves obtained in such investigations is the large number of critical points which they show, and in consequence of this, the interpretation of the results presents considerable difficulty. There appear to be many more potentials which represent critical stages in the production of radiation than can be accounted for by the ionization of the successive shells of the bombarded atoms. Moreover, where an element has been examined by several investigators, the results obtained are not satisfactorily concordant either as regards the number of critical points found within any given voltage range, or as regards the actual values of critical points. Dr. Andrewes, working with the authors, has examined a series of seven elements of consecutive atomic numbers, Cr (24), Mn (25), Fe (26), Co (27), Ni (28), Cu (29), Zn (30), over a voltage range extending from 0-230. Some of these elements have been examined by other investigators, some of whom (Thomas, Rollefson, Richardson and Chalklin) have recorded many more critical points in their curves than were obtained by Dr. Andrewes and the authors. The fact that different investigations yield very different results as regards number of critical points indicated, suggests at once that in the cases where only a few indications are obtained only the more fundamental types of atomic disturbances are being effected, and that in the other cases the experimental conditions are such as to facilitate a greater variety of atomic disturbances. The intensity of the bombarding electron stream is a factor which might be expected to influence the variety of disturbances possible, very considerably, and in the experiments of Thomas and of Rollefson the intensity of the bombarding electron stream was certainly considerably greater than in the experiments of Dr. Andrewes and the writers.

In the later of the two papers previously referred to, the authors have discussed the question of a possible explanation of the several points they obtained for each element, and the correlation between these points and X-ray levels. They have shown that for all the elements they investigated, critical points falling within the range of those found must be associated with the M shell of electrons. Employing X-ray data for the heavier elements, and for the light elements in so far as data were available, and extrapolating in the case of elements where X-ray measurements had not been made, reasons were given for selecting particular critical points for each element as corresponding to the  $M_I$  and  $M_{II, III}$  absorption limits of those elements, an absorption edge being taken to correspond to a displacement of an electron from its usual shell to the first possible unoccupied (or virtual) orbit. It was argued that there might be critical points at voltages somewhat higher than those corresponding to absorption edges, at which electrons from the shells concerned might be removed to successively more distant virtual orbits until actual ionization of the shells occurred.

For convenience of reference the values of the critical potentials found in the experiments referred to are given below in tabular form. The figures in the different vertical columns  $a$ ,  $b$ ,  $c$ , etc. indicate what the authors took to be corresponding critical points for the different elements in interpreting their results.

TABLE I.  
*Critical potentials (volts).*

	<i>g.</i>	<i>f.</i>	<i>e.</i>	<i>d.</i>	<i>c.</i>	<i>b.</i>	<i>a.</i>
Cr (24).....	...	60	70	...	143	160	173
Mn (25) .....	...	68	83	100	152	174	184
Fe (26).....	47	73	90	106	166	181	...
Co (27).....	...	...	94	113	171	191	...
Ni (28).....	...	...	104	...	178	196	...
Cu (29) .....	...	...	112	...	193	206	...
Zn (30).....	...	...	119	...	200	214	...

In an extension of the investigation, at present in progress, using a modification in the method of measurement of the radiation current, indications of critical potentials in the lower region of the curves, corresponding to the  $g$  and  $f$  points for iron, have been obtained with the other targets. As the investigation is not yet completed, and as in the light of these newer indications some modifications may be necessary

in the correlation of the various critical points in different elements, the additional values are not included in Table I.

By plotting the  $\sqrt{(\nu/R)}$  values of the voltages given in the table against the atomic numbers of the elements, and by constructing the  $\sqrt{(\nu/R)}$  against atomic number curves for various X-ray levels, and differences of X-ray levels, from X-ray line and absorption edge measurements, the value in the *g* column was shown to be that most nearly corresponding to a displacement to the periphery of the atom, of an electron from the group associated with the  $M_{II}$ ,  $III$  level, while the values in column *d* were shown to be those most nearly corresponding to similar transitions from the electron group associated with the level  $M_I$ . In the case of the  $M_{II}$ ,  $III$  level, the correlation could be made directly as the requisite X-ray line measurements were available for the elements in question. In the case of the  $M_I$  level, the correlation had to be made by extrapolation from X-ray data extending only down to atomic number 37. From the sequence of the points *g*, *f*, and *e*, and of the points *d*, *c*, and *b*, for iron, and by analogy for the other elements, it was suggested that the *g*, *f*, and *e* values were connected with displacements of an electron from the group associated with  $M_{II}$ ,  $III$  to different final positions, and the points *d*, *c*, *b*, and *a* with displacements to various final positions of an electron from the group associated with  $M_I$ .

Some precision X-ray measurements of certain L lines \* for some of the elements investigated by Dr. Andrewes and the authors, published since the date of their paper, make it now possible to calculate entirely from X-ray data the values of  $M_I - N_{II}$ ,  $III$  for these elements. These quantities cannot differ very much from the values of the energy of the first possible transition from the electron shells associated with  $M_I$  in the different atoms, and they show that the critical potentials given in column *e* of the table, rather than those in column *d*, are the ones which should be connected with such displacements, in spite of the fact that the *d* points rather than the *e* points appear to be most nearly in line with the corresponding values for heavier elements when extrapolating.

In a recent paper † Stoner has given a discussion of the significance of measurements of critical radiation potentials, by the method outlined, and he directs attention to the point that the extent of the voltage differences between the various

\* R. Thoræus, Phil. Mag. ser. 7, i. p. 312 (1926).

† E. C. Stoner, Phil. Mag. ser. 7, ii. p. 97 (1926).

critical stages which the authors associated with displacements of an electron from a particular shell to different final positions, is much larger than could be expected for such displacements in a neutral atom. It seems to be suggested in the paper referred to that if the principal and azimuthal quantum numbers of the deepest level to which an electron from an inner shell might be removed, were known, the exact extent of the voltage difference between the extreme critical potentials for different displacements of an electron from a particular shell in the neutral atom, could be calculated from the terms of the optical spectrum of that element. Though not themselves holding this view, the authors agree with Stoner in being of the opinion that the ranges of the different points associated in their paper with different displacements from particular shells, are too wide to be attributable to such displacements in neutral atoms, *i. e.* the difference between the critical points is too large for them to be identified with the "fine structure" of an X-ray absorption stage, predicted by Kossel.

The following considerations bear upon the question of the actual magnitude of the "fine structure" of an absorption stage. If an electron from the K shell of an atom is removed to the periphery of the atom, then, neglecting for the moment the question of selection principle rules in regard to transitions, one might expect that some indication of the new constitution of the outer part of the atom might be obtained by reference to the atomic structure of the element next higher in the order of atomic number. As regards the firmness of binding of electrons in the exterior parts of the atom, the effect of removing an electron from the K shell is practically the same as the effect of increasing the nuclear charge by one unit. Hence the electron removed from the K shell will occupy the most firmly bound position in the resulting system when it and the already existing valence electrons form a system similar to the system of outer electrons in the next higher element. In such a case the energy required to transfer the K electron from this position, and to detach it completely from the atom, would be practically the same as the energy corresponding to the ionizing potential of the next higher element (possibly very slightly less). Hence the "fine structure" of the K absorption edge attributable to displacements to virtual orbits in the neutral atom could not correspond to a voltage difference exceeding the ionizing potential of the next higher element.

That the screening action of electrons in other shells falls more and more short of perfect as we deal with shells

successively more distant from the nucleus in any atom is well established, and Turner has shown in a recent paper \* that the non-diagram X-ray lines related to  $K_{\alpha_1}$ , measured by Hjalmar † for certain light elements, admit of interpretation on the basis of Wentzel's theory of multiple ionization of the K and L shells in a way which, if the interpretation be correct, provides definite evidence that the removal of an L electron produces a smaller increase in the amount of energy required for the subsequent removal of an M electron than is produced by the removal of a K electron. It therefore seems reasonable to assume that the removal of an M electron increases the energy required for the subsequent removal of an N electron by a still smaller amount. Hence, if the M electron were removed merely to the nearest possible virtual orbit, the energy required subsequently to remove it completely from the atom would be less than would be required for the corresponding process in the case of an electron from the K shell. Therefore in a neutral atom the "fine structure" of an M absorption stage must correspond to a range of voltage quite definitely less than the ionizing potential of the next higher element.

If we attempt to predict from the selection rule governing changes of azimuthal quantum number, to which virtual orbits an electron ejected from any particular sub-group of electrons may go, we have to bear in mind not only the recent work of Heisenberg ‡ and of Hund § in regard to the term character of incomplete electron configurations, but also that the azimuthal quantum numbers ordinarily assigned to the various levels characterize the singly ionized shells, whereas in the initial stage of the transitions contemplated the shell is complete.

These considerations show the difficulties which would have to be overcome in any attempt to estimate from optical terms, either of the neutral or the ionized atom, exactly what "fine structure" to expect. Nevertheless, as has already been shown, we can, in cases where the optical data are available, or where the ionization potentials have been measured, obtain an upper limit which the extent of the "fine structure" cannot exceed in a system of any definite degree of ionization.

Stoner has suggested that some of the many critical points found in experiments of the type under consideration are

\* L. A. Turner, *Phys. Rev.* xxvi. p. 143 (1925).

† E. Hjalmar, *Zeit. f. Phys.* i. p. 439 (1920).

‡ W. Heisenberg, *Zeits. f. Phys.* xxxii. p. 841 (1925).

§ F. Hund, *Zeits. f. Phys.* xxxiii. p. 345 (1925).

accounted for by impacts which disturb electrons from the inner shells in atoms already singly, doubly, or trebly ionized in an optical sense. A difficulty in the way of accepting this explanation is that one would expect to be able to classify the points corresponding to any particular degree of optical ionization according to the intensities of the effects produced at the critical stages, because the proportions of atoms in the bombarded surface existing at any instant in the various degrees of ionization would be likely to be very different. In the experiments of Dr. Andrewes and the authors it did not appear that a classification of points on such a basis could be made. It seems to the writers more probable that the electron impacting on any given atom with energy sufficient for the purpose, might itself produce a certain degree of optical ionization in addition to disturbing an electron from an inner level of the atom. Such occurrences would give a wider range of voltages to be associated with any given degree of optical ionization than would be given by the bombardment of already ionized atoms, and they would not necessarily give bends in the curves of very different orders of magnitude according to the degree of ionization, because the greater multiplicity of the disturbing effects produced on the atom would result in the emission of more radiation quanta in the process of reorganization of the atom, the higher the degree of optical ionization produced, and this would tend to compensate for the possible less frequent occurrence of the more complicated disturbances.

Instances of the detection of critical potentials corresponding to the simultaneous removal of more than one electron from an atom are well known, *e.g.*, the double ionization potential of helium, 78.8 volts. Other instances of the occurrence of multiple effects at single impacts are to be found in the results of investigations of the potentials necessary for the production of spark lines of the spectra of the rare gases.

To quote a definite instance for the upper limit of the order of magnitude of the difference of the critical potentials possibly associated with the disturbance of any particular electron in an atom in a given state of optical ionization :— The ionizing potential of Mn (25) is 7.4 volts\*. Therefore if we disturbed a K electron in Cr (24), taking it first to the lowest possible virtual orbit, and then removing it completely, the final process would not require more than 7.4 volts. Similarly if we disturbed in the same two stages a K electron in a chromium atom which had already lost its outermost electron, the final process would not require more energy

\* M. A. Catalan, Phil. Trans. Roy. Soc. A, ccxxiii. p. 127 (1923).

than that corresponding to the ionization potential of singly ionized manganese, *i. e.*,  $14.5 \pm 0.4$  volts \*. Since to remove the most loosely attached electron from a normal chromium atom requires 6.8 volts, the potential difference required to give the energy necessary to remove at one electron impact the outermost electron and an electron from the K shell would differ very little from  $(6.8 + V + 14.5 \pm 0.4)$  volts, where  $V$  denotes the voltage required for the removal of the electron from the K shell to the lowest virtual orbit. As Stoner has pointed out, the energy necessary for such a transition will vary very little with the removal of outer electrons. Hence  $(6.8 + 14.5 \pm 0.4)$  volts is the maximum difference of the critical potentials which might be associated with transitions of a K electron in a chromium atom without assuming a higher state of optical ionization than the first. The corresponding difference for transitions of an M electron in a chromium atom would, of course, be likely to be less than this, but this may be taken as an upper limit. If we assume that the upper limit for the corresponding differences in the other elements is of the same order of magnitude, we see that the  $d$  points might conceivably be connected with the  $e$  points in this way, *i. e.*, that the  $e$  points correspond to the removal of an electron from a group associated with  $M_I$  to the periphery of a neutral atom, while the  $d$  points correspond to the complete removal of such an electron simultaneously with the removal of one of the most loosely bound electrons.

Whether the  $f$  points correspond to the complete removal of an electron from the group associated with  $M_{II}$ ,  $III$  simultaneously with the removal of an optical electron is uncertain, since the values for the other elements corresponding to the  $g$  value for iron, were not indicated in the curves. In the case of iron the difference between the two lowest points is 26 volts, whereas the difference between the  $d$  and  $e$  points is only 16 volts. Such a large discrepancy as this makes it doubtful whether we can justifiably assume  $g$  and  $f$  to be related similarly to the points  $e$  and  $d$ . Possibly the  $f$  points correspond to the removal of an  $M_{II}$ ,  $III$  electron simultaneously with the removal of more than one optical electron, though in this case it is difficult to see why the curves do not give indications of the removal of an  $M_{II}$ ,  $III$  electron simultaneously with the removal of one optical electron.

Considering the  $a$ ,  $b$ , and  $c$  points, it does not seem that they can be explained in any simple way on the basis of higher stages of optical ionization. Stoner has suggested that they are due to multiple impacts, *i. e.* an electron hitting first one

\* D. R. Hartree, 'Nature,' cxvi. p. 356 (1925).

atom and disturbing it, and then disturbing another atom with the energy retained after the first collision. In regard to this suggestion, the objection might again be urged that the indications of such occurrences would be expected to be very much less marked than the indications of events involving only single impacts.

The order of magnitude of the  $a$ ,  $b$ , and  $c$  values in relation to the lower values is such that they might be due to multiple disturbance of the M shell by single electron impacts, either the disturbance of two electrons from the sub-group associated with  $M_{II}$ ,  $III$  or the disturbance of one from each of the sub-groups associated with  $M_{II}$ ,  $III$  and  $M_I$ , or even possibly the disturbance of two electrons from among those associated with  $M_I$ . Evidence of the production of atoms multiply disturbed in their X-ray levels is to be found in the non-diagram X-ray lines which Wentzel has shown can be satisfactorily explained on the basis of states of multiple ionization of the inner region of the atom. In a recent letter to 'Nature,' Robinson\* records the production of different lines in the magnetic spectrum of the electrons emitted from a target exposed to X-rays when internal absorption by the atoms of the target, of the K radiations excited in them by absorption of the primary radiation, takes place. These lines he attributes to the ejection of L electrons from atoms in which the L shell is already ionized. Robinson states that he has so far obtained no evidence of the production of multiple ionization by a single X-ray quantum, but it does not follow that the effects obtainable by electron bombardment would be limited to those corresponding to the effects produced by X-ray absorption, so that the lack of evidence of multiple X-ray ionization by a single quantum does not invalidate the suggestion that such a process may occur as the result of electron impacts†.

If multiple ionization of an atom can take place as the result of absorption of a single quantum, then it is possible that some of the critical points obtained by various investigators are due to the occurrence of this effect in the electrode exposed to the radiation emitted by the target. As the energy of the bombarding electrons increases, the quality of the general X-radiation varies, and it is possible that at

\* H. Robinson, 'Nature,' cxviii. p. 224 (1926).

† The experiments of Siegbahn and Larsson on the voltages necessary for the excitation of the satellites of the  $L_\alpha$  line for molybdenum seem to provide evidence that the simultaneous disturbance of two electrons from X-ray levels by a single electron impact does occur (Sci. Abs. 577 1925).

certain values of the accelerating potential the general radiation is able to eject two or more electrons from the illuminated electrode by the absorption of individual quanta. Such occurrences would be expected to cause the appearance of discontinuities in the radiation curves. Effects of this kind might be described as discontinuities in the photo-electric current due to the general radiation, as distinct from discontinuities in the general radiation itself, suggested by Richardson and Chalklin. It would appear, however, that in experiments involving the use of several targets in turn, it should be possible to distinguish between discontinuities due to this cause and those characteristic of the target under test, because those produced by changes in the action of the general radiation on the electrode exposed to it should appear at the same voltages in the curves for all the targets. The absence of discontinuities common to all the targets may be taken as evidence of the non-occurrence of effects of the type discussed, and also, in conjunction with the many critical points which have been obtained, as indicating that many more types of atomic disturbance can be produced by electron impacts at suitable voltages, than by exposure to radiations of corresponding frequencies.

This raises an interesting point in connexion with the interpretation of results obtained in the "magnetic spectrum" method of investigation of X-ray levels, and the possibilities of the method in regard to the unravelling of the more complicated phenomena. In the case of multiple ionization by a single X-ray quantum, the determination of the amount of energy actually involved in the ejection of each electron might be a matter of very considerable difficulty, for the manner of distribution of the excess energy of the quantum above that required for the actual removal of the two electrons would not be known, and it might be very difficult to recognize which pairs of lines in the magnetic spectrum should be considered together. In the case of internal absorption of one of the characteristic wave-lengths by an atom already ionized in one of its inner shells, the determination of the energy value of the level in such an atom would follow directly from the difference between the energy of the characteristic radiation absorbed and that of the electrons giving the line in the magnetic spectrum. Hence, if we take the view that multiple ionization by absorption of single quanta does not occur \*, the results of investigations

\* D. Coster and J. H. van der Tuuk in a recent paper in the *Zeits. f. Phys.* (xxxvii. p. 367, 1926) have concluded that transferences of two or more electrons simultaneously appear to play no part in X-ray absorption spectra.

of energy level values by determining, by the method of magnetic bending, the energies of the electrons emitted from a target of the material irradiated by X-rays of known frequency, may be expected to be more easily interpreted, and to yield more direct values than the results of investigations of critical potentials for the production of radiation, though up to the present time the former method does not appear to have been developed for use in connexion with the accurate determination of the levels of relatively low energy value.

The very factor which puts the critical potential method at a disadvantage as regards the determination of the normal X-ray level values of atoms—namely the greater variety of atomic disturbances produced by electron impact—constitutes a strong reason for the further development of that method, in that it promises a means of obtaining information unobtainable by the other method, when once ways of facilitating the interpretation of the results are devised. A possible method whereby the identification of the nature of the atomic disturbances produced at the various critical stages might be achieved, would appear to be by combining with the location of critical points a determination of the distribution of velocities among the photoelectrons emitted by the radiation produced just above and just below each one.

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*CXX. Dimensional Analysis Again.**By P. W. BRIDGMAN\*.*

THE subject of dimensional analysis has been so much discussed in the pages of the *Philosophical Magazine* in the last few years that one would like to see it die a natural death, were it not that in the last two communications† things have taken such a turn that an unchallenged acceptance of the views there presented may easily affect the use which the physicist makes of this analysis.

My position on this general subject has already been expounded in considerable length and detail in my book ‘*Dimensional Analysis*,’ Yale University Press, 1922. This book was written primarily because there was nowhere any previous attempt to give a systematic examination of the arguments on which the dimensional method rests, nor

\* Communicated by the Author.

† Mrs. T. Ehrenfest-Afanassjewa, *Phil. Mag.* [7] i. pp. 257-272 (1926); Norman Campbell, *Phil. Mag.* [7] i. pp. 1145-1151 (1926).

to show how it may be applied in many of the cases of practice, although the dimensional method was used to a greater or less degree by nearly every physicist, and there were incomplete and incidental references to the theory in a great many places. Now in these previous incomplete references were contained many misconceptions and fallacies; it was the first task of the book to show what these fallacies were. Among these fallacies was the idea that an equation expressing a connexion between physical things must be dimensionally homogeneous. I then showed that, in spite of the unsatisfactory form in which the dimensional argument had been often stated, it was possible to put it on a thoroughly sound basis, and apply the method with confidence to the solution of many important problems. I particularly stressed the point that the method, when properly understood, has nothing esoteric about it, that it gives no information which we did not have already in a less available form, and that therefore an adequate physical grasp of each individual problem is necessary. No refinement of mathematical argument will give correct results if our physical grasp of the broad features of the problem is inadequate. Just here is the feature in which my treatment differed most from those preceding; I emphasized that the broad physical grasp necessary to an application of the method finds expression in a knowledge of the *general character* of the equations which govern the motion of the system. Only in this way could the puzzling matter of dimensional constants be satisfactorily treated. Thus if the problem is one involving fluid motion, as in discussing airplane problems, the governing equations are those of hydrodynamics, into which no dimensional constants enter, so that no such constant enters the final result; but if the problem is one of electrodynamics, the field equations of electrodynamics govern, which do contain a dimensional constant (velocity of light, or ratio of units), and the dimensional constant may be expected in the final result.

For the method, purged from many previous fallacies and made (comparatively) rigorous, I used the name "Dimensional Analysis." Now it is gratifying that the name has apparently been accepted, as shown by the titles of recent papers, but, unfortunately, not in the sense in which I used it, but with a more or less indefinite blend of many former misconceptions. Thus Mrs. Ehrenfest-Afanassjewa in particular, although generously attributing the name to me, ascribes to the "dimensional analysist" a miscellaneous assortment of errors, which even I, in my enthusiasm in my

book for putting the worst light on previous misconceptions, would hardly have ventured to attach to any individual. Thus she begins by committing the dimensional analyst to the thesis that all equations expressing physical relations are dimensionally homogeneous, which is supposed to be equivalent to the statement that dimensional constants cannot occur. She then allows him to talk the most meaningless nonsense about other possible universes in which the gravitational constant might be different from ours, and she ends by making him so blind in his resolution to use only a pure dimensional method that he forgets that he knows that the gravitational attraction of the earth varies inversely as the square of the distance, and so is unable to find how the period of a pendulum varies with the distance from the earth's centre.

Of course Mrs. Ehrenfest-Afanassjewa has no trouble in making merry with her poor analyst. Now comes the important point for the physicist. Because of these difficulties, she would have us abandon the dimensional method altogether, and substitute for it another, which she calls the theory of similitudes, much more mathematical in character, and much more difficult for the physicist to apply, as one may see on reading her treatment of the simple pendulum problem. There are many formal resemblances between the methods, as she points out, but that they are not the same is shown by the fact that they do not always give the same solutions. The method of similitudes resembles that of dimensional analysis as expounded in my book in that the important role of the fundamental equations governing the motion of the system is recognized, but there is a vital difference in that her method demands a knowledge of the equations in *detail*, whereas the dimensional method needs to know only the general character of the equations. It is well known that the dimensional method has its most important practical application in such complicated problems as that of the airplane, where it is hopeless to attempt to write the equations in detail. I do not see how Mrs. Ehrenfest-Afanassjewa's method can be applied to this problem at all. On the other hand, dimensional analysis, in the sense expounded in my book, can certainly solve all the problems which she gives to show the limitations of dimensional analysis, and she will further find in my book an explanation, on purely dimensional grounds, of the questions raised in the correspondence between Lord Rayleigh and Riabouchinsky which she discusses in her paper from the standpoint of her theory.

The main purpose of this note is then to dispute the conclusion that might be drawn from an unchallenged acceptance of Mrs. Ehrenfest-Afanassjewa's paper. I believe that the dimensional method *can* be made rigorous, that it is *not* necessary to replace it by the mathematical method of similitudes which she offers, that the dimensional method is much easier for the physicist to apply, and in many important practical cases is more powerful.

Opposed to Mrs. Ehrenfest-Afanassjewa is Norman Campbell, who will have none of her method of similitude, but prefers that of dimensions. However, I cannot agree with Campbell, as it seems to me that his argument is put on an incorrect basis. It is certainly not necessary to assume that physically similar systems are possible in order to apply the dimensional method. For example, the deduction of the relation between the mass of an electron, its charge, radius, and velocity of light (dimensional constant of the electrodynamic equations) does not involve the assumption at all that more than one kind of electron is physically possible. Neither is it necessary in deducing the pendulum formula to so far analyse the situation as to recognize that "the period of the pendulum seems to be the physical sum of elementary periods, during each of which it may be supposed to move with constant acceleration." I fear that if as deep an analysis as this were necessary, few physicists would ever have the courage to attempt a dimensional analysis at all.

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CXXI. *The Atomic Structure of AgMg and AuZn.* By  
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**I**N a previous paper the authors gave an account of the determination of the atomic structure of the two intermetallic compounds  $Mg_2Si$  and  $AlSb$ †, which were examined by the X-ray spectrometer. The present paper is a continuation of this work and contains the data obtained and the structure deduced therefrom, of the compounds  $AgMg$  and  $AuZn$ . The former was examined both with the spectrometer and by the photographic method. A full account of the procedure with the spectrometer will be found in previous papers‡. For the photographic method a Müller camera

\* Communicated by the Authors.

† Proc. Phys. Soc. xxxvi. Pt. 5, p. 341 (1924).

‡ See Proc. Phys. Soc. xxxv. p. 101 (1923); xxxvi. p. 14 (1923);  
xxxvi. p. 49 (1923).

was employed, the material under examination being reduced to a fine powder and rotated in a beam of X-rays from a copper target.

### (1) *AgMg.*

The curve obtained with the ionization method is shown in fig. 1, the radiation employed being the K-series radiation of a molybdenum target. The analysis is given in Table I.

Fig. 1.

AgMg. Centred cube. Side = 3.28 Å. Molybdenum Radiation.

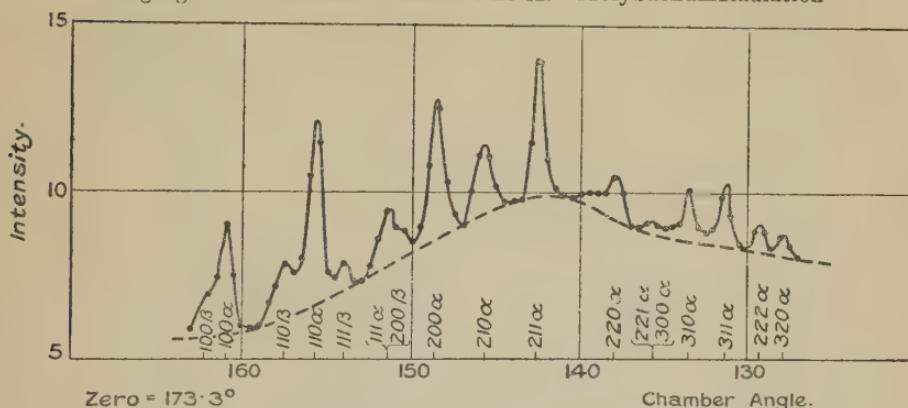


TABLE I.—AgMg plate. Molybdenum K radiation,  
 $\lambda_{\alpha} = 0.708 \text{ \AA}$ ,  $\lambda_{\beta} = 0.630 \text{ \AA}$ .

$\theta.$	Sin $\theta.$	Form.	$\lambda.$	$\alpha.$	I obs.	I calc.
5.55	0.0967	100	$\beta$	3.26 Å	8	8
6.15	0.1072	100	$\alpha$	3.30	30	23
7.90	0.1374	110	$\beta$	3.24	20	19
8.80	0.1530	110	$\alpha$	3.27	55	56
9.65	0.1677	111	$\beta$	3.26	8	3
10.95	0.1900	111	$\alpha$	3.23	10	9
11.25	0.1951	200	$\beta$	3.23	9	4
12.30	0.2130	200	$\alpha$	3.32	40	13
13.75	0.2376	{ 210 211	$\alpha$	3.33	10	13
15.35	0.2647	211	$\beta$	3.25	13	11
17.70	0.3040	220	$\alpha$	3.29	15	11
18.75	0.3214	{ 221 300	$\alpha$	3.30	2	6
19.90	0.3404	310	$\alpha$	3.29	12	16
21.00	0.3584	311	$\alpha$	3.28	18	6
22.00	0.3746	222	$\alpha$	3.27	6	5
22.70	0.3859	{ 320 400	$\alpha$	3.31	5	5
			$\beta$	3.27		

Mean value of  $\alpha = 3.28 \text{ \AA}$

The lines are all accounted for by a simple cubic structure of parameter 3.28 Å. The density of the material was directly determined and yielded the value 6.2 grammes per c.cm. The cube root of the molecular volume is 3.275 Å, and there are therefore one atom of silver and one of magnesium associated with the unit. The fifth column in Table I. gives the intensities of the lines as observed. In estimating the observed intensities a smooth curve (shown dotted in fig. 1) is drawn touching the lowest part of the observed curve. The heights of the peaks above this smooth curve are taken as the intensities of the different lines. The last column of Table I. gives the relative intensities of the lines calculated on the assumption that the structure is of the caesium chloride type, *i. e.*, that the atoms are assembled on a body-centred lattice. In the computation of the intensities the expression

$$I \propto j \left( \frac{d_{hkl}}{n} \right)^{2.35} \cdot A^2$$

has been employed,  $n$  being the order of the spectrum,  $j$  the number of cooperating planes,  $d_{hkl}$  the spacing of the plane whose indices are  $(hkl)$ , and  $A = 59$  or  $35$  according as  $n(h+k+l)$  is even or odd,  $59$  being the sum of and  $35$  the difference between the atomic numbers of silver ( $47$ ) and magnesium ( $12$ ). The agreement between observed and calculated intensities is probably as good as can be expected.

TABLE II.  
Powdered AgMg. Copper K radiation,  
 $\lambda_\alpha = 1.537 \text{ \AA}$ ,  $\lambda_\beta = 1.389 \text{ \AA}$ .

$\theta.$	Sin $\theta.$	Form.	$\lambda.$	$\alpha.$	I.
13.80	0.2385	100	$\alpha$	3.22 $\text{\AA}$	s
17.75	0.305	110	$\beta$	3.24	m
19.55	0.335	110	$\alpha$	3.24	vs
28.00	0.4695	200	$\alpha$	3.27	s
31.50	0.5525	210	$\alpha$	3.29	s
35.10	0.575	211	$\alpha$	3.27	vs
41.45	0.662	220	$\alpha$	3.27	m
44.65	0.703	{ 221 } 300 }	$\alpha$	3.28	m
47.30	0.735	310	$\alpha$	3.30	s
50.20	0.768	320	$\beta$	3.29	vvf
51.95	0.787	311	$\alpha$	3.24	vvf
53.90	0.808	222	$\alpha$	3.29	vvf
57.20	0.841	320	$\alpha$	3.30	vf
60.45	0.870	321	$\alpha$	3.30	s

Mean value of  $\alpha = 3.27^\circ \text{ \AA}$

Several photographs of the material were taken by means of the Müller camera. The analysis of one photograph is given in Table II. and bears out the result obtained by means of the spectrometer.

A fact which emerged during the examination of the material by the spectrometer is that when the material is examined after being etched, a spectrum is obtained which corresponds to a face-centred cubic structure of side  $4\cdot076 \text{ \AA}$ . This figure is in approximate agreement with that given by McKeehan \* for the parameter of the silver lattice. The etch dissolves out the magnesium from the body-centred lattice, and the silver atoms recrystallize at room temperature on a face-centred lattice. A curve obtained with the spectrometer using the etched material is shown in fig. 2, and the result is analysed in Table III.

Fig. 2.

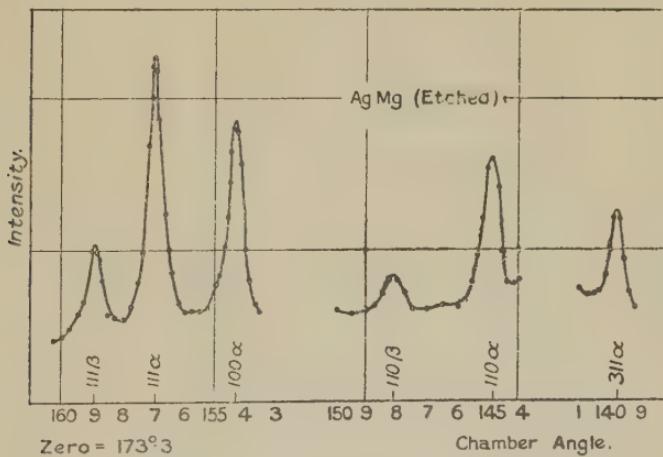


TABLE III.

Etched plate AgMg. Molybdenum K radiation,  
 $\lambda_\alpha = 0\cdot708 \text{ \AA}$ ,  $\lambda_\beta = 0\cdot630 \text{ \AA}$ .

$\theta.$	$\sin \theta.$	Form.	$\lambda.$	$a.$
7° 40'	0·1335	111	$\beta$	$4\cdot086 \text{ \AA}^{\circ}$
7 40	0·1507	111	$\alpha$	$4\cdot068$
10 0	0·1736	200	$\alpha$	$4\cdot079$
12 35	0·2178	220	$\beta$	$4\cdot090$
14 14	0·2459	220	$\alpha$	$4\cdot070$
16 47	0·2888	311	$\alpha$	$4\cdot065$

Mean value of  $a = 4\cdot076 \text{ \AA}^{\circ}$

\* Phys. Rev. xx, p. 424 (1922).

(2) *AuZn.\**

A small block of material of approximately the constitution AuZn was examined by the photographic method. The surface to be irradiated consisted of fairly large crystals, and was therefore rubbed on fine emery-cloth to break up the surface. The result of this treatment is to make the lines of the spectrum rather broad so that their position cannot be fixed with precision. The analysis of the photograph is given in Table IV., the observed lines being accounted for by a simple cubic structure of side 3·19 Å. The cube root of the molecular volume is 3·11, the observed density being 14·4 grammes per c.cm. As in the case of AgMg, there are therefore two atoms in the unit. The relative intensities of the lines are in accordance with a caesium chloride structure.

TABLE IV.  
Powdered AuZn. Copper radiation,  
 $\lambda_a = 1\cdot537 \text{ \AA}$ ,  $\lambda_b = 1\cdot389 \text{ \AA}$ .

$\theta.$	sin $\theta.$	Form.	$\lambda.$	$\alpha.$	I obs.	I calc.
14·05	0·244	100	$\alpha$	3·15 $\text{\AA}$	f	10
17·8	0·306	110	$\beta$	3·23	m	15
19·9	0·340	110	$\alpha$	3·22	s	44
24·9	0·421	111	$\alpha$	3·16	f	4
28·5	0·477	200	$\alpha$	3·22	f	10
32·0	0·530	210	$\alpha$	3·24	vf	6
36·25	0·591	211	$\alpha$	3·19	s	24
43·2	0·684	220	$\alpha$	3·18	f	9
61·5	0·879	320	$\alpha$	3·15	f	2

Mean value of  $\alpha = 3\cdot19 \text{ \AA}$ .

*Summary.*

The atomic structure of the two compounds AgMg and AuZn has been examined by X-ray methods. In each case the structure turns out to be of the caesium chloride type, the parameter AgMg being 3·28 Å and that of AuZn, 3·19 Å.

\* See Westgren and Phragmén, Phil. Mag. I. p. 311 (1925).

CXXII. *On the Condenser-Telephone.**To the Editors of the Philosophical Magazine.*

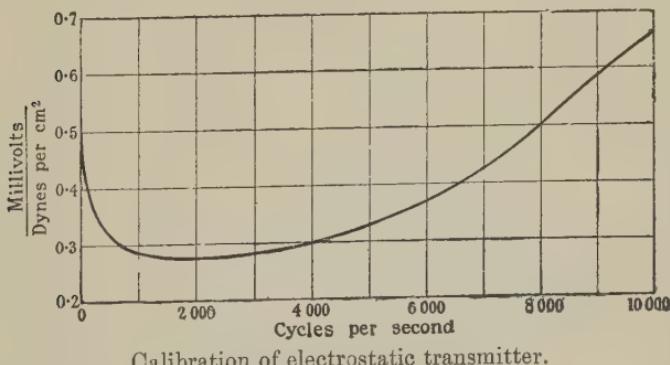
GENTLEMEN,—

**I**N the Phil. Mag. ser. 7, vol. ii. No. 9, September 1926 Dr. G. Green has a paper on Condenser-Telephones in which he works out their behaviour over the audio frequency band from fundamental data.

At first sight the results are somewhat perplexing, particularly to those who make use of the condenser-telephone for electro-acoustic measurement purposes.

Dr. Green shows that a small capacity condenser-transmitter such as the well-known Wente type used under the conditions he postulates would be inefficient at the lower audio frequencies. On the other hand, the Wente transmitter and most other types of condenser-transmitters under normal conditions of use have frequency-amplitude characteristics which invariably indicate a rising efficiency towards the lower end of the audio-frequency band.

The explanation lies in the circuit used by Dr. Green for his calculations. This circuit includes a transformer, and a value of inductance of the order of 0·8 henry is assumed.



Calibration of electrostatic transmitter.

Such a transformer is quite unsuitable to use as coupler between a condenser-transmitter and the grid of an amplifying valve, and, in practice, a condenser-transmitter is generally coupled to the grid of the first amplifying valve by an inductionless circuit. Under this condition the frequency-amplitude characteristic will be found to fall steadily from a maximum at low audio frequencies, and in

the case of transmitters of the Wente type with stretched diaphragms having natural periods towards the upper ends of the audio-frequency band, the characteristic will again rise towards this higher frequency. As an example, the calibration of a Wente electrostatic transmitter is reproduced\*.

It is thought advisable to draw attention to this apparent contradiction. Dr. Green's paper really deals with the operation of a condenser-telephone with a special and very unsuitable form of coupling so far as low capacity types of instrument are concerned.

Yours faithfully,

September 25, 1926.

B. S. COHEN, M.I.E.E.

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CXIII. *Luminous Discharge in a Rapidly Alternating Field.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

MAY I be permitted to draw attention to an error which Messrs. Gill and Donaldson have made, in their criticism of my method of measurement to which I made reference in an earlier letter (*Phil. Mag.* vol. ii. p. 741, 1926). These authors are of the opinion that the cathode stream instrument I have employed "only measures the electric force. .... When the discharge is passing the electric force is not uniform." May I in this connexion quote a sentence from my previous letter: "My method involves the measurement of the deflexion of an independent cathode stream in a high vacuum.". That is, the cathode stream does not pass through the discharge tube at all, but through a separate *high vacuum*, the experimental arrangement being described in detail in my paper in the *Annal. d. Physik* (vol. lxxvii. p. 287, 1925). It is obvious that in a high vacuum, where no discharge exists, the electric force between two parallel electrodes cannot be other than uniform, and therefore my cathode stream instrument measures not only the electric force, but the actual potential.

Yours faithfully,

München,  
October 14, 1926.

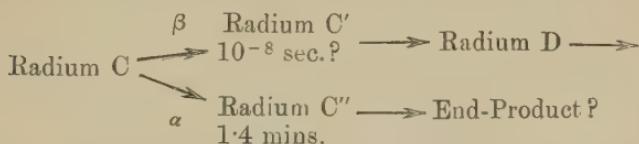
FRITZ KIRCHNER.

\* Physical Review, 1917, vol. x. p. 22, and 1922, vol. xix. p. 498. See also paper on Frequency Characteristics of Telephone Apparatus read before I.E.E. April 29th, 1926.

CXXIV. *On the Existence and Half-Period of Radium C.*  
*By A. W. BARTON, M.A., B.Sc., Trinity College,  
Cambridge\*.*

*Introductory.*

SINCE Radium C emits both  $\alpha$  and  $\beta$  rays it was inferred that it consists of two or more radio-active elements, and in 1909 Hahn and Meitner † obtained by recoil from it minute quantities of a new element Radium C''. The investigation was continued by Fajans ‡, who suggested the following scheme for the disintegration of radium C :—



Radium C appears to disintegrate in two different ways, 99.97 per cent. of the atoms emitting a  $\beta$ -particle to become Radium C' and 0.03 per cent. emitting an  $\alpha$ -particle to become Radium C''. Radium C' was not isolated, its existence being only inferred ; and furthermore the value of its half-period, if it does exist, is very hypothetical as it was calculated from the range of the  $\alpha$ -particles it emits using the Geiger-Nuttall Relation. This relation between the range of the  $\alpha$ -particles emitted by a radio-active element and its decay constant has been shown to be only approximately true by the accurate redetermination by Geiger of the ranges of the  $\alpha$ -particles emitted by various elements §. The consequent necessity for direct evidence on the existence and half-period of radium C' has been rendered still more urgent by the discovery || that radium C emits a few  $\alpha$ -particles of longer range than those already known. This may mean that radium C is still more complex than indicated by the above scheme of disintegration.

Any direct method for investigating the existence of radium C' and obtaining a rough value of its half-period depends upon obtaining an efficient  $\beta$ -ray recoil to separate the radium C' from radium C. Consequently, an investigation of the conditions most favourable to this recoil was

\* Communicated by Prof. Sir E. Rutherford, O.M., F.R.S.

† *Phys. Zeits.* x. p. 697 (1909).

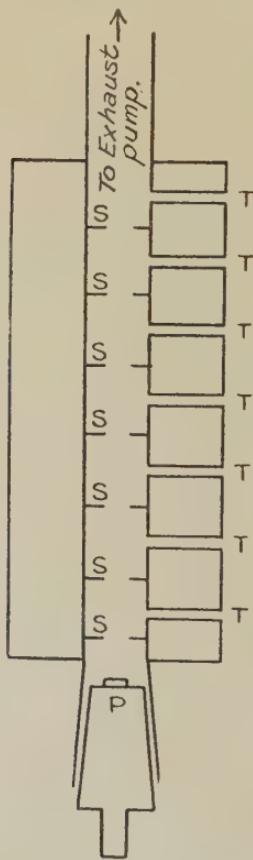
‡ *Phys. Zeits.* xii. p. 319 (1911); xiii. p. 699 (1912).

§ *Zeits. f. Physik*, viii. p. 45 (1921).

|| Proc. Roy. Soc. A, cv. p. 97 (1924).

undertaken with a view to applying the results to this problem \*. During these experiments an account of a beautiful method of isolating radium C' and finding its half-period was published by Jacobsen †. He found that radium C' exists and has a half-period of  $5 \times 10^{-5}$  sec., a value which does not agree with that obtained from the Geiger-Nuttall Relation. It would appear, however, that Jacobsen's experiments are open to criticism in certain respects, which will now be dealt with.

Fig. 1.



Apparatus used by Jacobsen.

His method of experiment was to project a beam of radium C' atoms limited by the screens S from the radium C on the plate P by  $\beta$ -ray recoil, the whole apparatus being exhausted to a pressure of  $10^{-4}$  mm. of mercury (fig. 1).

\* Phil. Mag. i. p. 835 (1926).

† Phil. Mag. xlvi. p. 23 (1924).

Owing to the very short half-period of radium C', a large proportion of the atoms disintegrate in passing down the tube, and by counting the number of  $\alpha$ -particles per minute striking a zinc-blende screen placed opposite the tubes T in succession the half-period of radium C' can be determined, assuming a value for the velocity of the recoil atoms. In order to be sure that the  $\alpha$ -particles so counted are due to the disintegration of radium C' and not to spurious effects such as scattering or "contamination," a count is taken with the pressure in the apparatus at about 5 mm. of mercury to stop the radium C' atoms, and the number so obtained subtracted from the corresponding value with the pressure at  $10^{-4}$  mm. There are, it would seem, three objections to this method of carrying out the experiment:—

- (1) Some of the  $\alpha$ -particles counted in the tube nearest to the plate D may be due to scattering.
- (2) The method of testing that the  $\alpha$ -particles counted are due to the disintegration of radium C' is unsatisfactory, as an increase of pressure would effect contamination and possibly other spurious effects.
- (3) An efficiency of recoil of 2 per cent. would be required to obtain the actual effects quoted in Jacobsen's paper. That this has never been previously obtained under the conditions he used constitutes the chief objection to accepting his results as final.

It seemed advisable to repeat this experiment chiefly because of the great importance of the problem itself, at the same time endeavouring to eliminate as far as possible the features criticised above in Jacobsen's method and also increasing the magnitude of the effects observed for a given amount of radium C.

#### *Principle of the Method.*

The principle of the method adopted in the present experiments is identical with that due to Jacobsen, but the dimensions of the apparatus were fixed so that for a given source of radium C four times as many  $\alpha$ -particles would be obtained in these experiments as in his work. Since it is essential to obtain as efficient a recoil as possible, the source of radium C must be prepared with great care, avoiding all traces of tarnishing and surface contamination.

A number of unsuccessful experiments was made with Von Lerch's method, using a nickel plate on which to deposit the radium C; but it was found that the best surface was obtained by depositing the radium C on a piece of platinum foil by electrolysis. This method of preparing a source of radium C is quite efficient and so the details of the method, which was worked out under the direction of Dr. R. G. Dickinson, of the Pasadena Institute, California, are given below, as it does not appear to have been used before.

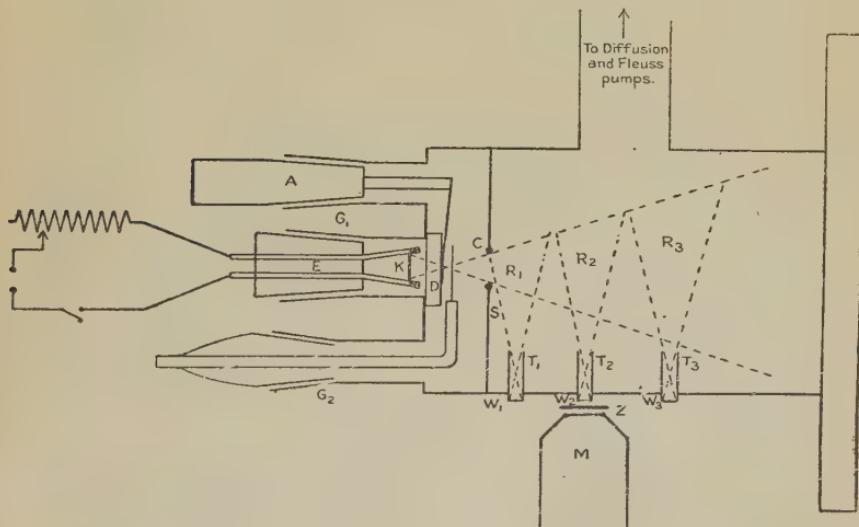
#### *Preparation of the Source of Radium C.*

Radium active deposit is obtained on the walls of a thin glass tube by exposing it to radium emanation for four hours, after which the tube is broken up and the active deposit is dissolved in about 5 c.c. of 20 per cent. hydrochloric acid. The platinum foil, 2 mm.  $\times$  6 mm., on which the radium C is to be deposited, dips into this solution and forms the cathode of a voltameter, the anode being in a separate vessel. After allowing 25 minutes for most of the radium A to decay away, the solution is heated to 80° C. and stirred by rotating the cathode itself, and the electrolysis is then started. The value of the current is adjusted so that the P.D. between the cathode and a calomel electrode in 20 per cent. hydrochloric acid is not numerically greater than -0·4 volt. If this value is exceeded, a sensible amount of radium B is deposited on the cathode. The electrolysis is allowed to proceed for 10 mins., when the cathode is removed from the solution, the current being switched off by this removal itself; otherwise a considerable amount of radium C would go into solution again, owing to the cathode being left for a short time in the hot hydrochloric acid with no current flowing. The source is then washed in distilled water and dried by a clean filter-paper; the surface of the platinum shows no trace of tarnish whatever and is as clean and bright as at the commencement of the electrolysis. Under these conditions a source of radium C containing only  $\frac{1}{3}$  per cent. of radium B can be obtained, as much as 60 per cent. of the radium C present in the solution being obtained on a piece of platinum foil of the above dimensions. It is essential that the volume of the solution of the active deposit be not greater than about 5 c.c. and that the P.D. between the cathode and the calomel electrode should be numerically less than -0·4 volt.

*The Experiments to Determine the Half-Period of Radium C.*

The apparatus finally used in these experiments is shown in fig. 2. It consists essentially of a brass box about 6·0 cm. long with a square cross-section, one side being pierced by three tubes  $T_1$ ,  $T_2$ ,  $T_3$ , each closed by a mica window  $W_1$ ,  $W_2$ , and  $W_3$ , respectively. A microscope  $M$  carrying a zinc-blende screen  $Z$  can be brought opposite any one tube at will, and is used to count the number of  $\alpha$ -particles issuing per minute from that tube.

Fig. 2.



The source of radium C prepared as above is screwed to two brass rods passing through the ground ebonite stopper E and inserted in the apparatus, which is then exhausted to a pressure of less than  $10^{-4}$  mm. of mercury by a two-stage diffusion pump backed by a Fleuss pump. At this pressure the mean free path of radium C' atoms is much greater than 6 cm., and so they can travel to the end of the box without collision. The source is then disconnected from the rest of the apparatus by turning the valve D by means of the ground metal joint A into the position shown, and it is then heated electrically to about  $400^\circ$  C. for some 30 secs. Previous experiments by the author on  $\beta$ -ray recoil have shown that this heating in a vacuum produces the conditions giving maximum efficiency of recoil \*.

\* Phil. Mag. i. p. 835 (1926).

A simple test experiment showed that the valve D, although not absolutely gas-tight, was quite adequate to prevent any serious increase in contamination. The communication between the source and the apparatus being restored, a beam of radium C' atoms with a constant solid angle defined by a circular hole in the screen S now passes down the apparatus. The average velocity of these atoms is of the order of  $10^5$  cm. per sec., and assuming that the half-period of radium C' is  $10^{-5}$  sec., it is evident that the number of atoms in the beam crossing any given plane perpendicular to it in one second is just one half that crossing a parallel plane one centimetre nearer the source in one second. Thus the number of atoms in a given length of the beam decreases rapidly with distance from the source, and the relation between these two quantities is found by counting the number of  $\alpha$ -particles per minute impinging on a zinc-blende screen placed in turn opposite the tubes T<sub>1</sub>, T<sub>2</sub>, and T<sub>3</sub>, correcting them for the decay of the radium C source. For the number of  $\alpha$ -particles per minute falling on the screen when opposite, say, the tube T<sub>2</sub> is proportional to the number of radium C' atoms breaking down in the region R<sub>2</sub> and so to the number present in that region. The number of radium C' atoms in a given region of the beam and the distance from the centre of that region to the source are now known. The latter quantity can be converted into time assuming the velocity of the recoil atoms, and so the decay of radium C' can be studied and its half-period determined. This method is admittedly not so precise as that due to Jacobsen, since the regions R are bigger than the corresponding regions in his experiments; but the above scheme was adopted in order to increase the effects obtained. The inaccuracy introduced in this way, however, is much less than that due to the variation of the velocity of the recoil atoms, which affects both sets of experiments.

In the present apparatus no  $\alpha$ -particles emitted directly from the source K can pass through the tubes T<sub>2</sub> and T<sub>3</sub> without being scattered at least twice, and their velocity would then be insufficient to enable them to penetrate the mica windows W<sub>2</sub> and W<sub>3</sub> of 4 cm. air equivalent closing these tubes. Again, if an  $\alpha$ -particle from the source were scattered through a suitable angle, about 90°, at the edge of the circular hole in the screen S, it could pass straight through the tube T<sub>1</sub>. But by lining the hole with carbon the velocity of the scattered  $\alpha$ -particle corresponds to a range of about 3 cm. of air, and so it cannot penetrate the mica window W of 4 cm. of air equivalent. Thus none of the  $\alpha$ -particles

counted in these experiments can be due to scattering ; this was confirmed by subsidiary experiments.

Finally, it is necessary to know the number of  $\alpha$ -particles at each tube due to contamination and any other spurious effects which may have been overlooked. This was determined by rotating a mica screen of 1 cm. air equivalent in front of the source by the ground glass joint  $G_2$ . This screen stops the beam of recoil atoms completely, and so any  $\alpha$ -particles counted now are due to spurious effects. The number so obtained when subtracted from the number counted with the source uncovered by the screen gives the number of  $\alpha$ -particles due to the disintegration of radium C'.

The advantages of these experiments over Jacobsen's method are :

- (1) The entire elimination of scattering.
- (2) The way in which the number of  $\alpha$ -particles due to spurious effects is estimated.

The number of  $\alpha$ -particles per min. per mg. of radium C to be expected at  $T_1$  is 20, assuming an efficiency of recoil of 0.5 per cent. As sources up to 5 mgs. were available, it should be possible to obtain quite definite evidence as to the existence and half-period of radium C'.

### *Results.*

The magnitude of the effects obtained in these experiments was not nearly so large as was expected ; this was probably due to low efficiency of recoil, as it is impossible to prevent considerable fluctuations in its value. The experiments were still further complicated by contamination, which often masked the effect of radium C' and rendered many of the experiments inconclusive. Contamination could not be prevented by cutting off the communication between the source and the box by a collodion film, say, for any such film will stop the stream of radium C' atoms. But a sufficient number of successful experiments was performed to show quite definitely that radium C' exists and to enable its half-period to be determined.

The existence of radium C' is proved if the number of  $\alpha$ -particles per minute at  $T_1$  is distinctly greater with the source uncovered by the mica screen than when covered. This was found to be the case in nine experiments, the ratio of the number with the source uncovered to that with it

covered varying from 2:1 to 5:1. The details of one of these experiments are appended :—

Number of $\alpha$ particles per min.	
Source uncovered.	Source covered.
36	9
22	2
9	3
5	0
9	2

The results of this experiment show quite clearly that radium C' exists, and this is confirmed by the other experiments. The sudden decrease in the numbers at the third count is due to the fact that a considerable time (about 30 mins.) elapsed between it and the second count, during which observations were being taken at tubes T<sub>2</sub> and T<sub>3</sub>.

In most of these experiments contamination at the tubes T<sub>2</sub> and T<sub>3</sub> was relatively so large that no definite conclusions could be drawn as to the existence of radium C' opposite them, *i. e.* in the regions R<sub>2</sub> and R<sub>3</sub>. It must have been there, but the amount was so small as to be masked by the contamination. In two of the experiments, however, the effects were of such a magnitude relative to the inevitable contamination as to enable the half-period of radium C' to be determined. The details of these experiments are now given :—

Strength of radium C source at beginning of the first count = 9 mgs.

Average number of  $\alpha$ -particles counted per min. due to radium C' corrected for the decay of the radium C source at tubes T<sub>1</sub>, T<sub>2</sub>, and T<sub>3</sub> = 36, 19, and <3 respectively. (The average of 6 counts at T<sub>1</sub> and T<sub>2</sub>, and of 2 counts at T<sub>3</sub>.)

Number of radium C' atoms present in the regions R<sub>1</sub>, R<sub>2</sub>, and R<sub>3</sub> at any instant = 36, 19, and <3 respectively.

Now the distance from the centre of R<sub>1</sub> to the centres of R<sub>2</sub> and R<sub>3</sub> = 1.0 and 2.5 cm. respectively.

Time taken for radium C' to move from R<sub>1</sub> to R<sub>2</sub> and R<sub>3</sub> =  $2.5 \times 10^{-6}$  sec. and  $6.0 \times 10^{-6}$  sec. respectively, assuming the velocity of the recoil atoms to be  $4 \times 10^5$  cm. per sec.

Thus a decay curve may be drawn from the above data:—

Number of Atoms of Radium C'.	Time $10^{-6}$ sec.
36	0·0
19	2·5
< 3	6·0

The half-period calculated from this curve is  $2\cdot7 \times 10^{-6}$  sec. It is unfortunate that no value could be assigned with certainty to the amount of radium C' in the region  $R_3$ . The counts at the tube  $T_3$  were made after those at  $T_1$  and  $T_2$ , and the number of  $\alpha$ -particles due to radium C' to be expected was about 4 per min., which was too small to be detected with any certainty. The smallness is due to the decay of the radium C source and to the fact that the centre of the region  $R_3$  is 4 cm. from the source K, from which it follows that the amount of radium C' leaving the source has decayed to 1/16 of its initial value when it reaches the centre of  $R_3$ . This disadvantage of having the region  $R_3$  so far from the source was unavoidable if the size of the regions  $R_1$ ,  $R_2$ , and  $R_3$  was to be increased so as to make the effects obtained in these experiments larger than those in Jacobsen's work.

The value of the half-period obtained from the other experiment is  $3\cdot2 \times 10^{-6}$  sec., so that the mean of the two is  $3\cdot0 \times 10^{-6}$  sec. This agrees very well with Jacobsen's value, which is  $1\cdot5 \times 10^{-6}$  sec., if the velocity of the recoil atoms were taken to be  $4 \times 10^5$  cm. per sec., as in this work, instead of his value,  $8 \times 10^5$  cm. per sec. The value,  $4 \times 10^5$  cm. per sec., was chosen for two reasons. Firstly, Jacobsen's value is the maximum theoretical velocity of the recoil atoms corresponding to an electron emitted with a velocity of 0·998 c. It is quite certain that only a small fraction of the recoil atoms would have this velocity, and so it was discarded; it may also be mentioned that Jacobsen states in his paper that it is a somewhat arbitrary choice. Secondly, the velocity of the recoil atoms varies continuously from  $4 \times 10^4$  cm. per sec. to  $8 \times 10^5$  cm. per sec., and it seems most reasonable, therefore, to use the mean value of their velocity in calculating the half-period of radium C'. Now the number of recoil atoms with a given velocity will vary with that velocity in the same way as the number of electrons emitted from radium C varies with their velocity. Using the results obtained by Chadwick and Ellis\* for this distri-

\* Proc. Camb. Phil. Soc. xxi. p. 274 (1923).

bution, the mean value of the velocity of the recoil atoms works out to be  $4 \times 10^5$  cm. per sec.

These experiments, then, confirm Jacobsen's work as to the existence of radium C'. Although the observations are not so accurate as Jacobsen's, nor is the method itself so precise, yet the value of the half-period obtained in this work is probably as accurate as his value because of the great inaccuracy introduced by the uncertainty of the velocity of the recoil atoms.

### *Summary.*

The previous work of Fajans and Jacobsen on the existence and half-period of radium C' is discussed, and the importance of confirming Jacobsen's results is emphasized.

A repetition of Jacobsen's experiments with certain modifications is described.

The result of this work confirms Jacobsen's experiments—that is, radium C' does exist and its half-period is of the order of  $10^{-6}$  sec.

In conclusion I should like to express my sincere thanks to Prof. Sir Ernest Rutherford, O.M., P.R.S., for suggesting this problem and for his advice and encouragement while it was being carried out. I have to thank Mr. R. A. R. Tricker, Trinity College, Cambridge, for his assistance in the counting of the  $\alpha$ -particles. I am indebted to Mr. G. A. R. Crowe for preparing the Radium Active Deposit used in these experiments.

### CXXV. *The Loud-Speaker as a Source of Sound for Reverberation Work.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

I HAVE recently read a paper by Dr. A. H. Davis and Mr. N. Fleming, entitled "The Loud-Speaker as a Source of Sound for Reverberation Work," published in your issue for July 1926, and should be glad of the opportunity of commenting upon it so far as concerns two references to a work of my own, viz. "On the Degradation of Acoustical Energy," Proc. Roy. Soc. A, vol. cv. pp. 80, &c. (1924).

Dr. Davis deduces from his elegant experimental work

the conclusion that appreciable degradation does not exist within the particular range of frequencies and intensities which he investigated. The process of reasoning whereby he arrives at this conclusion is peculiar and interesting. In effect he says, correctly enough (pp. 55-57), "If I employ a microphone of constant sensitivity throughout its range of response and *if there be no degradation*, then two particular curves, which I shall take, should theoretically be of the same form."

He then continues, "I tried three microphones: The first two yielded curves of different forms, so that I discarded them; but the third did give me the two curves alike. *Therefore this microphone is of constant sensitivity, and further, as a necessary corollary, there is not any degradation.*"

As a matter of fact, there is good reason to suppose that the sensitivity of the type (electrostatic) of microphone in question decreases with increase of the effect which it indicates, and it is easy to see that the sense of this deviation is such as would tend to counterbalance degradation effects, and thus to render the two curves in question of the same shape. Dr. Davis apparently consents to this view so far as the microphone is concerned, as he impliedly acknowledges the tendency of the microphone response curve to deviate from the linear when he says (p. 53): "The e.m.f. generated by the electrostatic microphone is, for small amplitudes, directly proportional to the amplitude . . ." It is noteworthy that a "small" amplitude remains undefined, being presumably that for which the response of the microphone is linear, although personally I prefer to regard it as one at which degradation is negligible.

I refrain from further comment on the paper as a whole, as it does not elsewhere refer explicitly to work of my own, but I should like to call attention to the whole of the paragraph on page 58, commencing "In the present experiment . . ." and ending ". . . position of the microphone." In particular, the last two lines of the paragraph—"Thus, in all cases the e.m.f. gives a measure of the sound amplitude at the position of the microphone"—are, to my mind, merely a statement of what one means by a microphone.

I remain,

Yours faithfully,  
MORRIS HART.

Air Defence Experimental  
Establishment, Biggin Hill,  
Westerham, Kent.  
3rd November, 1926.

## CXXVI. Notices respecting New Books.

*The Progress of Atomic Theory.* By Dr. A. C. CREHORE.  
(Taylor & Francis. 12s. 6d. net.)

THE appearance of this collected account of a certain mode of envisaging the problem of atomic structure is welcome, as is any serious attempt made, even at the present day, to interpret the phenomena in a manner more in line with the classical electrodynamics. In fact, although the models here discussed are, of course, not reconcilable with those postulated in the present form of quantum theory, it is nevertheless of interest to know the results to which they lead when certain premises are applied from the start. The author is a very competent mathematician, and can be relied upon at all points to find the strict logical consequences of the starting-points of his investigations. Thus, even to the convinced supporter of the quantum foundation, the book will be found to be of value and to suggest much for thought, whether viewed as a thesis investigating further ways in which the classical theory can suggest possible models capable of covering certain restricted domains of experience, or looked upon with the intention of comparison with the advancing quantum. The printing and general form of the book reflect great credit on the publishers, and misprints seem to be extremely rare.

*The Thirteen Books of Euclid's Elements.* By T. L. HEATH.  
(Second Edition. Cambridge University Press, 1926. 3 volumes.  
£3 10s. 0d. net.)

THE present volumes constitute a second edition of the thirteen books of Euclid's Elements translated from the text of Heiberg, with an introduction and commentary by Sir Thomas Heath. The first edition appeared in 1908 and was received with great enthusiasm by a large body of readers.

It is admitted that Heiberg's text is by far the best. To his admirable translation Sir Thomas added elaborate notes, sometimes historical, sometimes geometrical. The result of his tremendous labours has been the appearance of the present comprehensive work. The second edition now under review has been very carefully revised, many paragraphs are re-written, and sometimes even a sequence of paragraphs. Several additions have been made, and perhaps the most interesting is the use of much new matter in the two Excursuses at the end of vol. 1, dealing with, in the first place, Pythagoras and the Pythagoreans, and secondly, popular names for Euclid's individual proportions, founded on such things as the shape of the figures drawn by Euclid to

illustrate them. An immense amount of research work must have been involved in getting such material together even for a few pages of text.

The same remark is true of the rest of the book, which is packed even more closely than before with paragraphs in smaller print, containing the most interesting historical information accessible nowhere else to English readers. In fact, distinguished as he is so uniquely as a mathematician and Greek scholar combined, the author is nevertheless a very remarkable historian. In the preface he lays stress on the fact that Euclid is the greatest mathematical work which has come to us in the past, quite apart from the question as to how it should be taught, or how such matters as the Axiom of Parallels should be treated. We should like to say that these three volumes will themselves long remain classical, for they have given us all that can be found from any source on the far history of one branch of mathematics, and in a critical manner of the deepest research.

It is hardly necessary to say that the printer's share in the publication is beyond praise, for the Cambridge University Press never deviates from the high standard of all the mathematical works it issues.

*Projective Geometry.* By C. V. DURELL. (Macmillan & Co., 1926.)

THIS volume is a sequel to the author's 'Modern Geometry,' which deals with the properties of triangles, pencils, and circles. It is an abbreviated form of 'A Course of Plane Geometry for Advanced Students, Part II.,' published in 1910. Certain re-arrangements of the material have been made, and a considerable number of riders have been added. The book indeed contains a very ample supply of riders which will make it especially valuable.

We shall look forward to welcoming the author's projected work, 'A Concise Geometrical Conics.' There is at present great need of a well-written book on this subject.

*Solutions of the Examples in a Treatise on Dynamics of a Particle and of Rigid Bodies.* By S. L. LONEY, M.A. (Cambridge University Press, 1926. 17s. 6d. net.)

THE present work consists of solutions to the examples in Professor Loney's well-known Treatise. No doubt a not inconsiderable number of those teachers and students who use this text-book will be glad to have at hand for reference the solutions as given. It should be particularly useful for those students who have to work alone, though for this class of reader the solutions may sometimes prove rather too sketchy.

*Photographic Photometry.* By G. M. B. DOBSON, I. O. GRIFFITH, and D. N. HARRISON. (Oxford, Clarendon Press. 7s. 6d. net.)

THIS work is described as a study of methods<sup>s</sup> of measuring radiation by photographic means. The old description of books as supplying a long-felt want can be applied with complete truth to this volume. Much of the work described has been the outcome of research investigations in the Clarendon Laboratory, in some cases very recent, and on the part of the writers themselves. It has, therefore, a strong meteorological bent; and this fact constitutes one of its real values, for it is in this department that most striking new photometric work is being mainly done at the present time. The list of those who have assisted the three authors, mentioned in the Preface, is a final guarantee that the work is completely authoritative everywhere. We can recommend it with confidence as a work which should rapidly prove essential to the library of any experimental physicist, and equally to the teacher of Physics whether in a School or University. Its outlook is physical, and not mathematical, throughout.

The form of the volume, as it leaves the Press, is very pleasing, and the Oxford University Press is to be congratulated on such an addition to its list.

*Early Medicine and Biological Sciences.* By R. T. GUNTHER, (Oxford University Press (Mr. Humphrey Milford), 1926. Pp. 247. 8vo. 7s. 6d. net.)

THIS volume is part of the author's larger book on 'Early Science in Oxford,' and has been re-issued by request without the plates so as to bring its cost within the reach of a larger number of students.

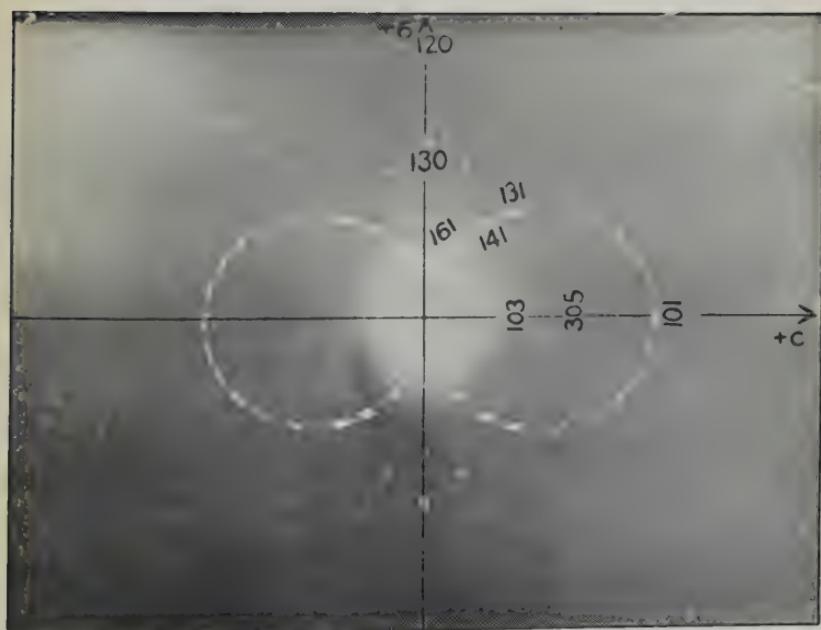
The work deals with early Medicine, Anatomy, Physiology, Zoology, Botany, and Geology, and though replete with historical data, is well and interestingly written. It is packed full of curious and out-of-the-way learning, and contains many striking illustrations and a few topical poems.

The story of Oxford's illustrious geologists introduces us to Hooke, Plot and his Theory of Fossils, Edward Lhwyd, "Strata Smith," Buckland (two poems and a picture describing his lectures), Sedgwick, Merchison, the great Lyell, and others—an imposing list of great masters of whom Oxford has a right to be proud.

This is a book which will appeal both to scholars and to dilettanti; it is both learned and amusing.



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CXXVII. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 750.]

May 5th, 1926.—Dr. F. A. Bather, F.R.S., President.  
in the Chair.**T**HE following communication was read:—

'The Geology of the District around Towyn and Abergynolwyn (Merioneth).' By Ralph Maurice Jehu, M.Sc., F.G.S.

The area investigated includes about 35 square miles of country, lying south-west of the Corris district, which has been recently described.<sup>1</sup> The rocks belong to the Bala and Valentian Series, and consist mainly of mudstones and shales with subordinate bands of grit. The lithological and faunal characters of the rocks are, on the whole, similar to those around Corris, so that the same classification and the same nomenclature have been retained so far as possible. The rocks of the Bala Series are described in detail.

The mapping of the various subdivisions has revealed the detailed structure of the area. The district is situated on the south-eastern flank of the Harlech Dome, so that, in general, the strata strike from south-west to north-east, and dip south-eastwards; but the area is crossed transversely by large anticlinal and synclinal folds, the axes of which trend north-north-eastwards in the south, and become north-and-south farther north. These transverse folds cause considerable deviation in the outcrops of the various rock-groups, and, within the major folds, there is evidence of minor folding.

The Bala or Tal-y-llyn Fault runs from south-west to north-east through the area, and is marked by the straight, steep-sided Tal-y-llyn Valley. There can be little doubt that this is a tear-fault with comparatively little vertical displacement; but, at present, it is impossible to state with any degree of precision the actual amount of lateral and vertical displacement. On the north side of the fault some seven main fold-axes have been recognized by Prof. A. H. Cox,<sup>2</sup> while on the south the author describes four main fold-axes. Difficulty is experienced when an attempt is made to correlate the structures on each side of the fault-line.

The southern part of the area is much affected by faulting, and three main groups of faults may be recognized: namely, (1) an east-and-west group; (2) a north-east and south-west group; and (3) a north-west and south-east group.

The rocks are highly cleaved, and the extraction of fossils is thereby rendered difficult. The strike of the cleavage-planes is approximately from south-west to north-east.

<sup>1</sup> W. J. Pugh, Q. J. G. S. vol. lxxix (1923) p. 508.<sup>2</sup> Q. J. G. S. vol. lxxxi (1925) p. 576.

## INDEX TO VOL. II.

---

**A**COUSTIC measurements, on the basis of, by reverberation methods, 543.  
 Adeney (Dr. W. E.) on the aeration of water under open-air conditions, 1140.  
 Air, on the Joule-Thomson effect for, 961; on the rate of solution of, in water, 1140.  
 Alkalies, on the magnetic susceptibilities of some, 21.  
 Alloys, on the thermoelectric properties of, 1188.  
 Alty (S.) on the effect of tension on the elastic properties of wires, 321.  
 Aluminium amalgams, on the conductivity of, 19.  
   — acetylacetone, on the crystal structure of, 1161.  
 Amalgams, on the resistivity and conductivity of dilute, 1; on the effect of a magnetic field on the resistance of, 176.  
 Andrews (J. P.) on an application of diffraction halos to elasticity, 945.  
 Anemometer, on the vane, 881.  
 Anhydrite, on the crystalline structure of, 114, 992.  
 Annular nozzles, on eddying flow from, 436.  
 Anodic polarization, on, 733.  
 Antimony amalgams, on the conductivity of, 17.  
 Arc, on the high vacuum, in hydrogen, 796.  
   — spectrum of potassium, on the, 1042.  
 Argon, on the scattering of positive rays by, 1076.  
 Atoms, on the distance between, in crystals, 258; on the electrical structure of, 1026.  
 Baker (J. F.) on the stresses in a spoked wheel under loads applied to the rim, 1234.  
 Banister (Dr. H.) on the transmission of sound through the head, 144; on the phase-effect and the localization of sound, 402.  
 Barkas (W. W.) on the photophoresis of colloidal particles in aqueous solutions, 1019.  
 Barkla (Prof. C. G.) on scattered X-rays and the J phenomenon, 642, 1116, 1122.  
 Barrel of an air-cooled cylinder, on temperature stresses and deflexions in the, 449.  
 Barton (A. W.) on the existence and half-period of radium C, 1273.  
 Bath for observations at low temperatures, on a, 383.  
 Beals (C. S.) on the spectrum of ionized silver, 770.  
 Benzoic acid, on the molecular association of, in benzene, 287.  
 Beryllium amalgams, on the conductivity of, 19.  
 Beta-rays, on the ranges of secondary, 1109.  
 Biggs (H. F.) on a simple exposition of electromagnetic relations, 1052.  
 Binks (W.) on the crystalline structure of anhydrite, 114.  
 Binnie (A. M.) on temperature stresses and deflexions in the fins and barrel of an air-cooled cylinder, 449.  
 Bircumshaw (L. L.) on the surface tension of liquid metals, 341.

Björnstähl (Y.) on electric double refraction in colloids, 701.

Books, new:—Crehore's The Progress of Atomic Theory, 1284; Jolly's Summation of Series, 496; Kaye & Laby's Four-Figure Mathematical Tables, 496; Bose's The Nervous Mechanism of Plants, 496.

Bowen (I.) on the effect of tension on the elastic properties of wires, 321.

Boys type of double resonator, on the, 751.

Bragg (Prof. W. L.) on interatomic distances in crystals, 258.

Bridgman (P. W.) on dimensional analysis, 1263.

Briggs (Dr. S. C.) on Werner's coordination theory and the electrical structure of the atom, 1026.

Browning (Dr. H. M.) on sound changes analyzed by records, 955.

Cadmium, on the structure of the resonance lines of, 611; on the fine structure of certain lines and energy levels of, 613.

Cæsium, on the magnetic susceptibility of, 21.

Calcium sulphate, on the crystalline structure of anhydrous, 114, 992.

Campbell (Dr. N. R.) on the variation of pressure with temperature in evacuated vessels, 369.

Carroll (M. F.) on molecular association and the equation of state, 385.

Cassen (B. M.) on the striated distribution of space charge, 948.

Catechol, on the crystal structure of, 1153.

Cathode, on the effect of the shape of the, on the glow discharge, 556.

— rays, on the radiation produced by, 678.

Cerium amalgams, on the conductivity of, 18.

Chadwick (Dr. J.) on the artificial disintegration of elements, 1056.

Chaplin (R.) on the adsorption of nitrogen at low pressures by activated charcoal, 1198.

Charcoal, on the adsorption of nitrogen by, 1198.

Circuits, on the general formulae for two syntonized coupled, 1098; on the resistance of high-frequency, 1213.

Clark (Dr. L. H.) on secondary radiations produced by gamma-rays, 783.

Cohen (B. S.) on the condenser-telephone, 1271.

Colloidal particles, on the photophoresis of, in aqueous solutions, 1019.

Colloids, on electric double refraction in, 701.

Compton effect and the reflexion of X-rays by crystals, on the, 657.

Condenser, on the parallel plate, 827.

Condenser-telephone, on the, 497, 1271.

Continuous medium in four-dimensional space, on the equilibrium and motion of a, 994.

Convergence of series, on the relation to physics of the notion of, 241.

Coordination compounds, on the atomic structure and magnetic properties of, 86.

— theory, on Werner's, 1026.

Copper, on the X-ray spectrum of, 1011; on the thermoelectric properties of solid solutions of, 1188.

— spectrum, on the analysis of the, 194.

Coupled circuits, on the general formulae for two syntonized, 1098.

Crystal lattice of metallic elements, on the, 1148.

— structure of certain compounds, on the, 1153.

Crystals, on interatomic distances in, 258; on the deformation of tungsten, 289; on the reflexion of X-rays by, 657.

Daniell (Dr. P. J.) on orthogonal potentials, 247.

Dauvillier (Dr. A.) on the electric discharge in gases, 1046.

Davies (Dr. A. C.) on critical potentials and X-ray term values, 1253.

Davis (Dr. A. H.) on the loud-speaker as a source of sound for reverberation work, 51; on the basis of acoustic measurements by reverberation methods, 543.

Density of fluids, on the, 1127.  
 Dickson (Dr. E. C. S.) on the crystalline structure of anhydrite, 114.  
 Dickson (T. W.) on the oblique rebound of a ball from a plane, 1091.  
 Diffraction halos, on an application of, to elasticity, 945.  
 Dimensional analysis, on, 1263.  
 Disintegration of elements, on the artificial, 1056.  
 Dobson, Griffith and Harrison's Photographic Photometry, 1286.  
 Donaldson (R. H.) on a new method of obtaining a luminous discharge in gases at low pressures, 129, 742.  
 Double refraction, on electric, in colloids, 701.  
 Durell's Projective Geometry, 1285.  
 Earth, on the surface history of the, 245, 1218.  
 Eckersley (T. L.) on the Compton scattering and the structure of radiation, 367.  
 Eclogite, on, as the substratum of the earth's crust, 1230.  
 Eddies, on the growth of, in a viscous fluid, 844.  
 Eddying flow from annular nozzles, on, 436.  
 Edwards (E.) on the effect of tension on the elastic properties of wires, 321.  
 Edwards (T. I.) on the resistivity and conductivity of dilute amalgams, 1.  
 Ehrenhaft (Prof. F.) on the determination of the size and weight of submicroscopic spheres, 30.  
 Elastic material, on a geometrical presentment of the constants of an, 588.  
 — properties of wires, on the effect of tension on the, 321.  
 — range of friction, on the, 806.  
 Elasticity, on the determination of the modulus of, by dynamical methods, 351; on an application of diffraction halos to, 945; on the coefficients of, for the solid state, 431.  
 Electric discharge in gases, on the, 913, 1046.  
 — double refraction in colloids, on, 701.  
 Electric resistance, on the, at fusion and the crystal lattice of metallic elements, 1148; on the, of high-frequency circuits, 1213.  
 Electrical structure of the atom, on the, 1026.  
 Electricity, on the radiation produced by the passage of, through gases, 674.  
 Electrolytes, on the Milner and Debye theories of strong, 577, 586.  
 Electromagnetic relations, on a simple exposition of, 1052.  
 Electrons and molecules, on the transference of energy in collisions between, 474.  
 Elements, on the artificial disintegration of, 1056.  
 Elles (Dr. G. L.) on the geology of Ben Lawers, 749.  
 Elliptic functions, on two-dimensional fields specified by, 827.  
 Engine cylinder, on the temperature stresses and deflexions in an air-cooled, 449.  
 Equation of state, on molecular association and the, 385.  
 Ethyl chloride, on the latent heat of vaporization of, 817.  
 Eumorfopoulos (N.) on the Joule-Thomson effect for air, 961.  
 Evacuated vessels, on the variation of pressure with temperature in, 369.  
 Evans (Dr. J.) on regions of compression, 748.  
 Explosions, on the shape of waves from large, 137.  
 Farnsides (Prof. W. G.) on the Cambrian slate-belt of Nantlle, 744.  
 Fins of an air-cooled cylinder, on temperature stresses and deflexions in the, 449.  
 Fleming (N.) on the loud-speaker as a source of sound for reverberation work, 51.  
 Flickers, on the theory of, in vision, 1170.  
 Flow, on irrotational, past two intersecting planes, 900.  
 Fluids, on the stability of layers of heated below, 833; on the growth of eddies in viscous, 844; on the density of, 1127.

Focken (C. M.) on the transference of energy in collisions between electrons and molecules, 474.

Four-dimensional space, on the equilibrium and motion of a continuous medium in, 994.

Friction, on the elastic range of, 806.

Gamma-rays, on secondary radiations produced by, 783.

Gases, luminous discharge in 743, 1272.

—, on a new method of obtaining a luminous discharge in, at low pressures, 129, 741, 742, 743; on the scattering of light in, 237; on the residual, in evacuated vessels, 369; on the transference of energy in collisions between electrons and molecules in, 474; on the high-frequency oscillatory discharge in rarefied, 508; on the radiation produced by the passage of electricity through, 674; on the electric discharge in, 1046; on the scattering of positive rays by, 1076.

Geological Society, proceedings of the, 744, 1287.

Germanium amalgams, on the conductivity of, 15.

Gill (E. W. B.) on a new method of obtaining a luminous discharge in gases at low pressures, 129, 742.

Glenday (V. G.) on the geology of the Suk Hills, 744.

Glow discharge, on the effect of the shape of the cathode on the, 556.

Gold, on the properties of colloidal, 38; on the arc spectrum of, 208; on electric double refraction in, 715; on the thermoelectric properties of solid solutions of, 1188; on the atomic structure of compounds of, and zinc, 1266.

— particles, on the size of colloidal, 1024.

Goucher (F. S.) on the deformation of tungsten single crystals, 289.

Granites, on the pre-Cambrian, 1218.

Gravity, on the action in parabolic paths under, 800.

Gray (Dr. R. C.) on the magnetic stability of permanent magnets, 521.

Green (Dr. G.) on the condenser telephone, 497.

Grumbach (Prof. A.) on the origin of the E.M.F. of a photoelectric cell, 313.

Guggenheim (E. A.) on the velocity constant of a unimolecular reaction, 538.

Gunther's Early Medicine and Biological Sciences, 1286.

Gwyther (R. F.) on a geometrical presentation of the constants of an elastic material, 588.

Halos, on an application of diffraction, to elasticity, 945.

Hart (M.) on the loud-speaker as a source of sound for reverberation work, 1282.

Hartley (H.) on the Milner and Debye theories of strong electrolytes, 586.

Haze, on the making of a salt, 1165.

Head, on the transmission of sound through the, 144.

Heat, on the nature of, 1006.

Heath's The thirteen Books of Euclid's Elements, 1284.

Helium, on absorption and resonance radiation in excited, 529; on the scattering of positive rays by, 1076.

Hicks (Prof. W. M.) on the analysis of the copper spectrum, 194.

High-frequency circuits, on the resistance of, 1213.

High resistances, on the calculation and application of, of small self-inductance, 65.

Holmes (Dr. A.) on the radioactivity of potassium and its geological significance, 1218.

Horton (Prof. F.) on critical potentials and X-ray term values, 1253.

Houston (Dr. R. A.) on the theory of the absorption of X-rays, 512.

Howland (R. C. J.) on the oblique rebound of a ball from a plane, 1091.

Hughes (Dr. E.) on the minimization of magnetic leakage, 162.

Hydrochloric acid, on the activity coefficients of aqueous, 1085.

Hydrogen, on a new method of producing a discharge in, 743; on the high vacuum arc in, 746.

Hydrogen line, on self-reversal of the red, 876.  
 Integrigraph, on a simple, 778.  
 Interatomic distances in crystals, on, 258.  
 Iron, on the water-spark absorption spectrum of, 742; on the thermo-electric properties of solid solutions of, 1188.  
 Irrotational flow past two intersecting planes, on, 900.  
**J** phenomenon, on the, 642, 1116, 1122.  
 Jackson (Dr. L. C.) on the atomic structure and magnetic properties of coordination compounds, 86.  
 Jeffreys (Dr. H.) on the relation to physics of the notion of convergence of series, 241; on the stability of a layer of fluid heated below, 833.  
 Jenkins (H. G.) on the nitrogen afterglow spectra, 621.  
 Jehu (R. M.) on the geology of the district around Towyn and Abergynolwyn, 287.  
 Johnson (Mrs. M. R.) on intensity variations in the spectrum of neon, 593.  
 Johnson (Dr. R. C.) on intensity variations in the spectrum of neon, 593 on the nitrogen afterglow spectra, 621.  
 Joly (Prof. J.) on the surface history of the earth, 245.  
 Jones (Miss P.) on the effect of a magnetic field on the resistance of mercury and some amalgams, 176.  
 Jones (T. J.) on the effect of a magnetic field on the resistance of mercury and some amalgams, 176.  
 Joule-Thomson effect for air, on the, 961.  
 Kasterin (Prof. N. P.) on Sir J. J. Thomson's model of a light-quantum, 1208.  
 Khastgir (Dr. S. R.) on scattered X-rays, 642.  
 Kirchner (Dr. F.) on a new method of obtaining a luminous discharge in gases at low pressures, 741; on the luminous discharge in an alternating field, 1272.  
 Kirkby (Rev. P. J.) on alternative currents in rarefied oxygen in the same circuit, 913.  
 Kunz (Dr. J.) on the scattering of light in gases, 237.  
 Lasareff (Prof. P.) on the theory of flickers in peripheral and central vision, 1170.  
 Latent heats of vaporization of ethyl and methyl chlorides, on the, 817.  
 Lawson (Dr. R. W.) on the radioactivity of potassium and its geological significance, 1218.  
 Lead, on the surface tension of liquid, 341; on the arc spectrum of, 633.  
 Legendre function of order  $-\frac{1}{2}$ , on the, 1184.  
 Levy (Prof. H.) on the growth of eddies in a viscous fluid, 844.  
 Light, on the scattering of, in gases, 237.  
 — quantum, on a simple, 1157; on Sir J. J. Thomson's model of a, 1208.  
 Loney's Solutions of the Examples in a Treatise on Dynamics of a Particle and of Rigid Bodies, 1285.  
 Loud-speaker, on the, as a source of sound for reverberation work, 51, 1282.  
 Lowry (H. V.) on the Legendre function of order  $-\frac{1}{2}$ , 1184.  
 Luminous discharge in gases at low pressures, on a new method of obtaining a, 129, 741, 742, 743, 1272.  
 Lunt (Dr. R. W.) on the current voltage characteristic of a Siemens ozonizer, 314; on a new method of producing a discharge in hydrogen, 743.  
 Lyman (Prof. T.) on an improved grating for vacuum spectrographs, 310.  
 McCurdy (Dr. W. H.) on absorption and resonance radiation in excited helium and the structure of the 3889 line, 529.  
 Mackenzie (Miss G. I.) on scattered X-rays, 1116.  
 Magnesium, on the atomic structure of compounds of silver and, 1266.  
 Magnetic field, on the effect of a, on the electrical resistance of mercury and some amalgams, 671.  
 — leakage, on the minimization of, 162.

Magnetic properties of coordination compounds, on the, 86.  
 — spectrum method of investigating X-ray levels, on the, 1262.  
 — susceptibilities of some alkalis, on the, 21.  
 Magnets, on the magnetic stability of permanent, 521.  
 Marr (Prof. J. E.) on the pleistocene deposits of the Ouse basin, 750.  
 Meksyn (D.) on the equilibrium and motion of a continuous medium in four-dimensional space, 994.  
 Mercury, on the resistivity and conductivity of, 1; on the effect of a magnetic field on the electrical conductivity of, 176; on electric double refraction in, 713.  
 — still, on a simple vacuum arc, 317.  
 Merton (Prof. T. R.) on reversal in vacuum tube spectra, 975.  
 Metallic elements, on the electric resistance at fusion and the crystal lattice of, 1148.  
 Metals, on the surface tension of liquid, 341.  
 Methyl chloride, on the latent heat of vaporization of, 817.  
 Molecular association and the equation of state, on, 385.  
 Molecules, on the transference of energy in collisions between electrons and, 474.  
 Morris (T. O.) on the Cambrian slate-belt of Nantlle, 744.  
 Morton (Prof. W. B.) on the action in parabolic paths under gravity, 800; on the parallel-plate condenser, 827; on irrotational flow past two intersecting planes, 900.  
 Neon, on intensity variations in the spectrum of, 593.  
 Newman (Prof. F. H.) on the high vacuum arc in hydrogen, 796; on the flash arc spectrum of potassium, 1042.  
 Nickel, on the X-ray spectrum of, 1011; on the thermoelectric properties of solid solutions of, 1188.  
 Nitrogen on the afterglow spectra of, 621; on the rate of solution of, in water, 1140; on the adsorption of, by activated charcoal, 1198.  
 Nonhebel (G.) on the Milner and Debye theories of strong electrolytes, 566; on the activity coefficients of dilute hydrochloric acid, 1085.  
 Norbury (Dr. A. L.) on the thermoelectric properties of metallic solid solutions, 1188.  
 Nozzles, on eddying flow from annular, 436.  
 Nuttal (J. M.) on the ranges of secondary beta-rays, 1109.  
 Oblique rebound, on the, of a ball from a plane, 1091.  
 Orifice flow as affected by viscosity and capillarity, on, 852.  
 Orthogonal potentials, on, 247.  
 Oscillations, on relaxation, 978.  
 Oscillatory discharge in rarefied gas, on the high frequency, 508.  
 Oxygen, on alternative currents in rarefied, in the same circuit, 913; on the scattering of positive rays by, 1076; on the rate of solution of, in water, 1140.  
 Owen (Dr. E. A.) on the atomic structure of AgMg and AuZn, 1266.  
 Owens (Dr. J. S.) on the making of a salt haze, 1165.  
 Ower (E.) on the vane anemometer, 881.  
 Ozonizer, on the current voltage characteristic of a Siemens, 314.  
 Palladium, on the thermoelectric properties of solid solutions of, 1188.  
 Parabolic paths, on the action in, under gravity, 800.  
 Particle and of Rigid Bodies, Dynamics of a, 1285.  
 Paris (Dr. E. T.) on the "Boys" type of double resonator, 751.  
 Parkinson (J.) on the geology of the Suk Hills, 744.  
 Patterson (W. H.) on a bath for observations at low temperatures, 383.  
 Perlitz (Dr. H.) on the electric resistance at fusion and the crystal lattice of metallic elements.  
 Permeameter, on a modified form of the Iliovici, 162.  
 Phase effect and the localization of sound, on the, 402.

Phosphor-bronze wires, on the effect of tension on the elastic properties of, 321.

Photoelectric action, on the distribution of energy among the electrons emitted from a plate by, 680.

—, on the origin of the E.M.F. of a, 313.

— emission from platinum, on the, 463.

Photophoresis of colloidal particles in aqueous solutions, on the, 1019.

Physics, on the relation to, of the notion of convergence of series, 241.

Pippard (Prof. A. J. S.) on the stresses in a spoked wheel under loads applied to the rim, 1234.

Planes, on irrotational flow past two intersecting, 900.

Platinum, on the photoelectric emission from, 463; on the thermoelectric properties of solid solutions of, 1188.

van der Pol (Dr. B., jr.) on relaxation oscillations, 978.

Polarization, on anodic, 733.

Positive column in oxygen, on the, 913.

— rays, on the radiation produced by, 678; on the scattering of, by gases, 1076.

Potassium, on the magnetic susceptibility of, 21; on the flash arc spectrum of, 1042; on the radioactivity of, 1218.

— ferricyanide, on the crystal structure of, 1156.

Potentials, on orthogonal, 247; on critical, and X-ray term values, 1253.

Press (Prof. A.) on the elasticity coefficients and the thermodynamic integration factor for the solid state, 431.

Pressure, on the variation of, with temperature in evacuated vessels, 369.

Preston (G. D.) on the atomic structure of AgMg and AuZn, 1266.

Quantum, on Sir J. J. Thomson's model of a light-, 1208.

Radiation, on the Compton scattering and the structure of, 267; on the, produced by the passage of electricity through gases, 674.

Radioactivity of potassium and rubidium, on the, 1218.

Radium C, on the half-period of, 1273.

Rai (J.) on the Joule-Thomson effect for air, 961.

Ramsey (Prof. R. R.) on the resistance of high-frequency circuits, 1213.

Rankin (J. S.) on the elastic range of friction, 806.

Reaction, on the velocity constant of a unimolecular, 538.

— constant equation, on the, 448.

Rebound, on the oblique, of a ball from a plane, 1091.

Relaxation oscillations, on, 978.

Resistances, on the calculation and application of high, of small self-inductance, 65.

Resonance lines, on the, of cadmium and zinc, 611.

— radiation of excited helium, on the, 529.

Resonator, on the Boys type of double, 751.

Reverberation methods, on the basis of acoustic measurements by, 543.

— work, on the loud-speaker as a source of sound for, 51, 1282.

Reversal in vacuum tube spectra, on, 975.

Richards (R. C.) on the high-frequency oscillatory discharge in rarefied gas, 508.

Richardson (Dr. E. G.) on eddying flow from annular nozzles, 436.

Robb (Dr. A. A.) on a simple integrator, 778.

Rubidium, on the magnetic susceptibility of, 21; on the radioactivity of, 1218.

Salt haze, on the making of a, 1165.

Sarkar (Dr. A. N.) on an X-ray examination of the crystal structure of certain compounds, 1153.

Scatward (G.) on the Milner and Debye theories of strong electrolytes, 577.

Searle (V. H. L.) on an oscillographic study of anodic polarization, 733.

Self-reversal of the red hydrogen line, on, 876.

Series, on the relation to physics of the notion of convergence of, 241.

Shand (Prof. J.) on the geology of Pilansberg, 747.

Shaxby (Dr. J. H.) on the density of fluids, 1127.

Sheppard (S. E.) on the reaction constant equation, 448.

Siemens ozonizer, on the current voltage characteristic of a, 314.

Silver, on the arc spectrum of, 207; on the spectrum of ionized, 770; on the thermoelectric properties of solid solutions of, 1188.

Silver, on the atomic structure of compounds of, and magnesium, 1266.

Sodium, on the magnetic susceptibility of, 21.

— chloride, on electric double refraction of, 727.

Solid solutions, on the thermoelectric properties of, 1188.

Sound, on the transmission of, through the head, 144; on the phase-effect and the localization of, 402.

— changes analyzed by records, 955.

Space charge, on the striated distribution of, 948.

Spectra, on reversal in vacuum tube, 975; on the X-ray, of the lower elements, 1007.

Spectrographs, on an improved grating for vacuum, 310.

Spectrum, on the analysis of the copper, 194; on intensity variations in the, of neon, 593; on the afterglow, of nitrogen, 621; on the arc, of lead, 633; on the, of ionized silver, 770; on the flash arc, of potassium, 1042.

Stability of a layer of fluid heated below, on the, 833.

Stephenson (W.) on the effect of the shape of the cathode on the glow discharge, 556.

Still, on a simple vacuum arc mercury, 317.

Stoner (Dr. E. C.) on X-ray term values, absorption limits, and critical potentials, 97.

Stresses in a spoked wheel, on the, 1234.

Striated distribution of space charge, on the, 948.

Submicroscopic spheres, on the determination of the size and weight of, 30.

Sucksmith (W.) on the magnetic susceptibilities of some alkalis, 21.

Sulphur, on electric double refraction in, 722.

Sur (A. K.) on the water-spark absorption spectrum of iron, 742.

Sur (N. K.) on the arc spectrum of lead, 633.

Surface tension of liquid metals, on the, 341.

Sutton (T. C.) on the shape of waves from large explosions, 137.

Swift (H. W.) on the determination of the modulus of elasticity by dynamical methods, 351; on orifice flow as affected by viscosity and capillarity, 852.

Telephone, on the condenser-, 497, 1271.

Thallium amalgams, on the conductivity of, 10.

Thermodynamic equation of state, on the, 431.

Thermoelectric properties of metallic solid solutions, on the, 1188.

Thomson (Prof. G. P.) on the scattering of positive rays by gases, 1076.

Thomson (Sir J. J.) on the radiation produced by the passage of electricity through gases, 674.

Thoræus (R.) on the X-ray spectra of the lower elements, 1007.

Tin, on the surface tension of liquid, 341.

Townsend (Prof. J. S.) on the transference of energy in collisions between electrons and molecules, 474.

Tungsten single crystals, on the deformation of, 289.

— wires, on the effect of tension on the elastic properties of, 321.

Tyler (E.) on eddying flow from annular nozzles, 436.

Ultraviolet light, on the production of real images of submicroscopic particles by means of, 30.

Unimolecular reaction, on the velocity constant of a, 538.

Vacuum spectrographs, on an improved grating for, 310.  
 — tube spectra, on reversal in, 975.  
 Vanadium, on the X-ray spectrum of, 1007.  
 Vane anemometer, on the, 881.  
 Velocity constant of a unimolecular reaction, on the, 538.  
 Violin, analysis of the sounds of the, 955.  
 Viscous fluid, on the growth of eddies in a, 844.  
 Vision, on the theory of flickers in, 1170.  
 Voice, analysis of the sounds of the, 955.  
 Waran (Prof. H. P.) on a simple vacuum are mercury still, 317.  
 Wasastjerna (Prof. J. A.) on the crystalline structure of anhydrite, 992.  
 Wasser (Dr. E.) on the determination of the size and weight of submicroscopic spheres, 30.  
 Water, on the aeration of, under open-air conditions, 1140.  
 Watson (Dr. W. H.) on the control of the J phenomenon, 1122.  
 Waves, on the shape of, from large explosions, 137.  
 Welo (Dr. L. A.) on the photoelectric emission from platinum, 463.  
 Werner's coordination theory, on, 1026.  
 Wheel, on the stresses in a spoked, 1234.  
 Whittaker (Prof. E. T.) on a simple light-quantum, 1137.  
 Wilcken (Dr. J. A.) on the molecular association of benzoic acid in benzene, 287.  
 Williams (E. J.) on the Compton effect and the reflexion of X-rays by crystals, 657; on the ranges of secondary beta rays, 1109.  
 Wilmette (R. M.) on high resistances of small self-inductance, 65; on general formulæ for two syntonized coupled circuits, 1098.  
 Wires, on the effect of tension on the elastic properties of, 321.  
 Wood (Prof. R. W.) on an improved grating for vacuum spectrographs, 310; on the structure of cadmium and zinc resonance lines, 611; on the self-reversal of the red hydrogen line, 876.  
 X-ray examination of the crystal structure of certain compounds, on the, 1153.  
 — spectra of the lower elements, on the, 1007.  
 — term values, on, 97, 1253.  
 X-rays, on the theory of the absorption of, 512; on scattered, 642, 1116, 1122; on the reflexion of, by crystals, 657; on the nature of soft, 1050.  
 Yates (G. W. C.) on the latent heats of vaporization of ethyl and methyl chlorides, 817.  
 Yttrium amalgams, on the conductivity of, 18.  
 Zinc, on the atomic structure of compounds of gold and, 1266.  
 —, on the X-ray spectrum of, 1011.  
 — resonance lines, on the structure of, 611.

END OF THE SECOND VOLUME.

48395